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Activation Analysis of Mercury

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For the activation analysis of mercury, Hg^{197}, with a 65 hr half-life, 68 keV X-quanta and 77 keV gamma quanta, has been selected. It was found that evaporation is serious even if certain precautions are taken. All samples were therefore sealed in quartz tubes. Gamma spectra were, after aging, recorded without breaking the tubes. The sensitivity limit is, at neutron flux 10^{12} n/cm^2 sec, about 0·03 μg. In the parts-per-million region and higher, a 5–10 per cent maximum error is typical. The method has been used since 1957 and has been applied to several hundred samples comprising biological tissue, blood, faeces, cellulose, paper, seed grains, pharmaceutical products, historical remains, aluminium and aluminium corrosion products. It is probably less practical than the gas spectrophotometric method for cellulose and water but might be a practical suggestion for biological samples and aluminium products and, of course, for various sorts of comparisons with other analytical methods for mercury at low levels.

L'ANALYSE PAR ACTIVATION DU MERCURE

Pour l'analyse par activation du mercure, on a choisi le Hg^{197} possédant: période de demi-valeur 65 hr quanta X 68 keV et quanta gamma 77 keV. On trouva que l'évaporation est grave même si on prend certaines précautions. Donc tous les échantillons furent scellés en tubes de quartz. Les spectres gamma furent enregistrés, après la période de viellissement, sans briser les tubes. La limite de sensibilité pour un flux de neutrons de 10^{12} n/cm^2 est environ 0,03 μg. Dans la région de parties-par-million ou plus, une erreur de 5 à 10 pour cent est typique. On emploie cette méthode depuis 1957, l'ayant appliquée à plusieurs centaines d'échantillons tels que le tissu biologique, le sang, l'excrément, la cellulose, le papier, les graines, les produits pharmaceutiques, les restes historiques, l'aluminium et les produits de la corrosion de l'aluminium. Elle est probablement moins praticable, pour la cellulose et l'eau, que la méthode spectrophotométrique à gaz, mais elle pourrait être praticable pour les échantillons biologiques et pour les produits d'aluminium et aussi, évidemment, pour des comparaisons diverses avec les autres méthodes analytiques pour le mercure en quantités minimantes.

АКТИВАЦИОННЫЙ АНАЛИЗ РТУТИ

Hg^{197} с периодом полураспада 65 часов и энергией X-квантов 68 кэв и гамма-квантов 77 кэв был выбран для активационного анализа. Было найдено, что даже если принять соответствующие меры предосторожности, происходит значительное испарение образцов. Поэтому все образцы были помещены в запаянные кварцевые трубки. По истечении некоторого периода, не разбивая трубок, снимали гамма-спектры. Предел чувствительности при потоке нейтронов 10^{12} н/см^2 сек составлял около 0,03 μg. Максимальная погрешность обычно была 5–10 процентов. Метод применялся с 1957 года и был испробован на нескольких сотнях образцов, включая биологические ткани, кровь, испражнения, целлюлозу, бумагу, семена растений, фармацевтические препараты, исторические находки, алюминий, и продукты коррозии алюминия. Для целлюлозы и воды данный метод вероятно менее практичен, чем газовая спектрофотометрия но он может оказаться полезным при исследовании биологических образцов и продуктов алюминия, а также, конечно, при сравнительной оценке других методов анализа ртути.

AKTIVIERUNGSANALYSE VON QUECKSILBER

Für die Aktivierungsanalyse von Quecksilber wurde Hg^{197} mit einer Halbwertszeit von 65 Std., 68 keV-Röntgenquanten und 77 keV γ-Quanten ausgewählt. Sogar unter Anwendung von Vorsichtsmassregeln spielt die Verdampfung eine bedeutende Rolle. Alle Proben wurden daher in Quarzröhrchen verschlossen. Nachdem man die Präparate bestimmte Zeiten abklingen liess, wurden die γ-Spektren ohne Öffnen der Röhrchen aufgenommen. Bei einem Neutronenflux von 10^{12} n/cm^2 sec liegt die Nachweisgrenze bei 0,03 μg. In der parts per Million Gegend und darüber ist ein maximaler Fehler von 5–10% typisch. Die seit 1957 gebrauchte Methode wurde bei mehreren 100 Proben von biologischem Gewebe, Blut, Exkrementen, Zellulose, Papier, Saatgut, pharmazeutischen Produkten, historischen Relikten, Aluminium und Aluminium-Korrosionsprodukten angewendet. Sie ist wahrscheinlich weniger praktisch als die gasspektrophotometrische Methode für Zellulose und Wasser, jedoch mag sie eine praktische Hilfe bei biologischen Proben und Aluminiumprodukten sein, sowie natürlich bei verschiedenen Vergleichen mit anderen analytischen Methoden für geringe Quecksilbermengen.

INTRODUCTION

With the advent of the nuclear reactor, much attention has been paid to the method of activation analysis by means of neutrons.[1] The orthodox method implies a chemical separation of certain elements after activation. Often it is possible, however, to omit the separation by taking advantage of the radiation properties and of the energy selectivity of certain detectors. This working procedure has been termed "non-destructive" by Leddicotte *et al.*[2] or it can be called "spectrometric".[3]

We have encountered the problem of assaying mercury in various kinds of samples including biological samples of various sorts, cellulose, metals, etc. and have examined the potentialities of activation analysis and especially the direct spectrometric technique. The use of the 68–77 keV roentgen-gamma line of 65 hr Hg^{197} was found appropriate and experience of several hundred samples has been accumulated since the middle of 1957. The method has so far been only briefly mentioned (see below). Details on cellulose and paper samples will be retained for another publication[5] together with Bethge.

NUCLEAR PHYSICAL FOUNDATIONS OF NEUTRON ACTIVATION OF MERCURY

Selection of method

When mercury of natural isotopic composition is subjected to neutron irradiation, the neutron capture reactions in Table 1 take place.

There are thus four main possibilities for performing activation analyses. (Excitation to Hg^{197} and Hg^{197m} is considered as one case here.) The use of the short-lived Hg^{199m} (42 min) or Hg^{205} (5·5 min) has the advantage of a short activation time but it seems very likely that their activities will be masked

Table 1. Neutron capture reactions of natural mercury

Reaction[6]	Half-life of capture product[6]	Cross-section for activation (barns) (at 2200 m/s)[7]	Activation cross-section of element (barns)
$Hg^{196}(n,\gamma)Hg^{197m}$	24 hr	3100 ± 1000	4·5
$Hg^{196}(n,\gamma)Hg^{197}$	65 hr		
$Hg^{198}(n,\gamma)Hg^{199m}$	42 min	—	
$Hg^{202}(n,\gamma)Hg^{203}$	46·9 days	3·8 ± 0·8	1·1
$Hg^{204}(n,\gamma)Hg^{205}$	5·5 min	0·43	0·03

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by other activities (such as Cl^{38} 37 min half-life, Mn^{56} 2·6 hr and also by K^{42} 12·5 hr, Cu^{64} 12·8 hr, Na^{24} 15·0 hr in several practical cases met by us). Thus, a direct spectrometric technique would be extremely difficult. On the other hand, if a rapid chemical or other separation is designed such as selective evaporation of mercury, one might find at least Hg^{199m} useful in future.

The selection between the use of Hg^{197} and Hg^{197m} on the one hand and Hg^{203} on the other is made by considering the respective activation cross-sections. It is seen (cf. Table 1) that the activation cross-section of forming Hg^{203} is 1·1 barns and that for Hg^{197} is 4·5 barns. The superiority of the latter is of course emphasized when the activation time is considered. Hg^{197} requires an activation time of a few days whereas Hg^{203} requires a few months to get a comparable degree of saturation.

As will be evident below, the use of Hg^{197} permits a direct spectrometric analysis with the sample contained in its envelope. It has been proved possible to age a number of disturbing activities present in our samples down to sufficiently low levels.

For these reasons, we have selected the reaction $Hg^{196}(n,\gamma)Hg^{197}$ as the most appropriate one for activation analysis.

Properties of Hg^{197m} *and* Hg^{197}

Since there are two nuclear isomers of Hg^{197}, their radiation properties, especially γ-transitions, and formation cross-sections have to be considered in order to select the best procedure for the measurements. The most energetic isomer, Hg^{197m} with 25 hr half-life, emits[6] a 133 keV gamma line and a weaker one of 164 keV. The other isomer, Hg^{197} with 65 hr half-life, emits after electron capture a 77 keV gamma line as well as some weaker lines.

The choice between Hg^{197m} and Hg^{197} is governed by two main questions: (i) what are the capture cross-sections leading directly to Hg^{197m} and to Hg^{197}? (ii) if the samples can be measured in the envelopes after aging, at what time after activation is it possible to perform the measurements?

No answer to the first question could apparently be found in the literature. A special study, to be published later, has therefore been initiated in this laboratory in order to elucidate it. Irradiations in the D_2O reactor R1 in Stockholm have, preliminarily, given the result that the cross-section leading to Hg^{197} is about a factor of a hundred larger than that leading to Hg^{197m}. Even though Hg^{197} is formed from the decay of Hg^{197m}, it is clear that, for activation purposes, Hg^{197} is the more preferable isotope.

The second question can be answered from a large number of practical activation cases. These show that the aging time should be 2–3 days or somewhat more in order to eliminate short-lived activities (listed above). At that time after reactor irradiation, Hg^{197} is the dominant isomer.

Thus, from both points of view, there are strong reasons for choosing Hg^{197} and even

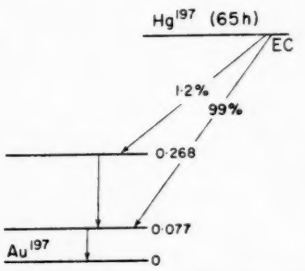

FIG. 1. Disintegration scheme of Hg^{197} taken from Reference (6) (neglecting Hg^{197m}). Numbers are in MeV.

for neglecting Hg^{197m} from the present analytical point of view. In the following, this choice was made throughout. The disintegration scheme of Hg^{197} is given in Fig. 1 (taken from [6]). The electromagnetic radiation emitted from Hg^{197} has now to be considered more closely. The components are: (a) the strong (99 per cent) gamma transition of Hg^{197} 77 keV, (b) X-rays following electron capture 68 keV and 10 keV. (Actually 68 keV is an average value of the two α-satellites. In addition there are beta and other lines of higher energy.) (c) A weaker (1·3 per cent) gamma transition of 191 keV.

The *K* fluorescence yield of the 68 keV

X-rays is estimated from published data[9] to be 95 per cent. The 77 keV is strongly converted and only about 30 per cent of the disintegration yields gamma rays. Thus, the intensity quotient 68 keV X-rays to 77 keV gammas should be about 3.

In the analytical procedure (see below) the gamma radiation in the vicinity of the 77 keV line and the *K* X-ray line of the standard and the sample are compared. Since it is of course improbable that a difference exists in any kind of radiation properties of the radioactive mercury due to different chemical states in sample and standard, this procedure is justified.

As the same nuclear state of Au^{197} is reached from the decay of Pt^{197} (18 hr), care must be paid to ensure that platinum is not present in the samples (see below). The formation cross-section of Pt^{197} calculated as natural platinum element is 0·28 barns[8] (thermal neutrons). After 65 hr aging, Pt^{197} has decayed to 10 per cent of its original value. From these data, it is evident that one part of mercury is equivalent to about forty parts of platinum from this point of view. The influence of Pt^{197} is then further reduced with continued aging. As an example, consider 1 μg of mercury in a sample; 40 μg of platinum would give the same activity. If the platinum content is less than 2 μg, the corresponding activity will be less than 5 per cent of the mercury activity in the example.

NEUTRON IRRADIATION

All irradiations have been performed in the pneumatic tube system of the heavy-water-moderated natural-uranium research reactor R1 in Stockholm[10] (the reactor is operated by AB Atomenergi and is situated about 500 m from our laboratory).

The positions used are at about one-third of peak flux which is about $2 \cdot 10^{12}$ n/cm² sec at 600 kW power. Thus we have used $6–7 \times 10^{11}$ n/cm² sec (thermal neutrons). The fast neutron flux does not interfere with the method as far as is known. This flux is stated to be about one tenth of the thermal flux.

In the method finally adopted (see below), samples and standards are always irradiated in quartz glass tubes. Usually seven tubes, diameter 8 mm, are placed together in an aluminium can of a standardized type (diameter 25 mm, length 65 mm).

There is some risk of errors due to different neutron fluxes. Obviously the ideal case is where sample and standard are situated in exactly the same flux. The flux topography within the channel must be considered in the regions used.[11] The steepest gradient is about 2·8 per cent/cm. Because sample and standard may be separated as much as 2 cm because of the tubes, the maximum error can be 5·6 per cent. However, the positions in the part of the channels passing the centre of the reactor have only 0·4 per cent/cm flux gradients, i.e. the maximum error is less than 1 per cent. Therefore, care is taken always to perform the activation in these positions.

Another phenomenon to be considered is the flux depression. A schematic representation is given in Fig. 2. The total flux

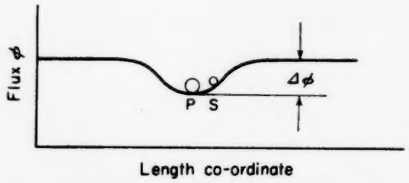

FIG. 2. Schematic representation of flux depression in a reactor. The sample, but not the standard, is assumed to be strongly neutron absorbent.

depression $\Delta\phi/\phi$ is an index for the difference of the flux at the sample and at the standard. From the figure, it is seen that the actual difference can be much smaller than the flux depression.

HUGHES[12] quotes theoretical results concerning the flux depression. The assumption behind that work is that the neutron-absorbing sample is thought of as a spherical shell (radius r_0) of a certain equivalent thickness (t) and placed in a diffusing neutron flux. The result is given as a factor R, i.e. ratio of

the flux at the foil to the flux without foil.

Rearranging gives (if flux depression is small):

$$\frac{\Delta\phi}{\phi} = \frac{3 \,.\, N \,.\, \sigma_a \,.\, t}{\lambda_{tr}/r_0 + \lambda_{tr}/L}.$$

Here N is the number of nuclei cm^3, σ_a is the absorption cross-section, λ_{tr} is the transport mean free path and L is the diffusion length of the neutron.

Despite the above-mentioned approximation, this formula should be able to yield the right order of magnitude of the flux depression according to HUGHES.[12]

As an example related to the present problem, we investigate the flux depression of 2 g of quartz glass containing 1 g of cellulose and 80 μg of mercury. The flux depression is estimated by means of the formula just mentioned to be about 0·3 per cent, i.e. very small. Even if this estimation is rough and even if we consider seven such tubes and the surrounding aluminium can, the conclusion that the depression errors will be small should indeed be valid. Of course, no strong neutron absorbers should be placed near the activation positions because they would give profound flux depressions and hence a steep unknown flux gradient in the activation tube.

Self-absorption of neutrons is another source of error which should not be confused with flux depression. Simple calculations using cross-section data on thermal neutron absorption for the case considered show that this error is less than 0·3 per cent. This source of error may be much more serious if resonance capture is important. Whether this is the case or not cannot be judged at present since it does not seem to be known whether the capture cross-section of Hg^{196} exhibits resonances. This question can be left, however, to experimental tests (see below).

In the case of neutron capture in a nuclide like Hg^{196} with its very large cross-section, the burn-out should be considered. This can be computed[14] using

$$N = N_0 e^{-\sigma_a \phi \,.\, t}.$$

Here t denotes the time and N_0 the number of Hg^{196} atoms from the start of irradiation.

At a flux of 10^{12} n/cm^2 sec, the burn-out is about 0·001 per cent/hr, i.e. ~0·1 per cent/70 hr, but at 10^{14} ~0·1 per cent/hr, i.e. about 7 per cent/70 hr. Thus there is no risk of a considerable error at 10^{12} n/cm^2 sec and, in such a case, the standard can be used several times, but it is seen that it should not be used too many times. It is seen that the problem is quite important in high-flux reactors and should be given serious attention. An unknown property is the cross-section for further capture from the radioactive Hg^{197}.

DETECTOR AND SPECTROMETRY

A scintillation spectrometer approach was chosen for the detection of the electromagnetic radiations from Hg^{197}. Since the energy is low, the Na(I)Tl crystal scintillation detector possesses several advantages. In the relevant energy region (50–100 keV), the efficiency of the detector is nearly 100 per cent (see for example BELL[15]). Moreover, almost all of this leads to photoelectric absorption.

A loss due to X-ray escape is always present and is pronounced in this energy region.[15] As is well known, the linearity of pulse height versus absorbed energy is very good. We have used a 3 × 3 in. NaI detector and have only occasionally made use of a 2 mm detector which has the same high efficiency but reduces the effect of high energy gamma radiation. The reason why the thin crystal was not always used is a practical one since an arrangement employing the thicker crystal was continuously available in our laboratory. The Hg^{197} spectrum was generally studied in the region 0–150 keV, after an appropriate aging time. This region is lower than the Compton distribution resulting from higher-energy gamma lines, and so the background is found to be flat or only slightly increasing with energy.

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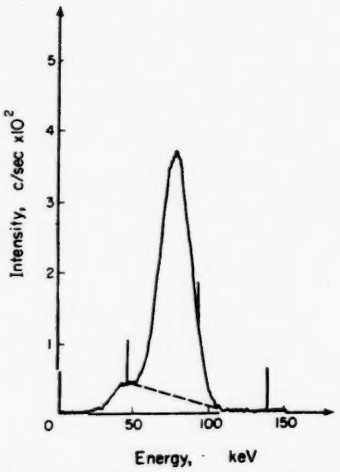

Fig. 3. Scintillation spectrum of Hg^{197} (65 hr) in the region 0–150 keV as detected by a 3 × 3 in. NaI(Tl) crystal. The sample was studied in a quartz glass envelope. Its contribution at the time of investigation was probably very low. The bump at the low energy side is due to *K*-escape in the crystal. The dotted line represents a suggested background drawing–it may however be possible to improve upon this representation.

The 68 keV X-rays and the 77 keV gamma line cannot be separated with the present scintillation spectrometry technique. A rather broad (half-width 25 per cent), but distinct, peak is obtained (Fig. 3) which is further broadened on the low-energy side obviously due to the escape phenomenon. The top of the photoelectric peak should be more close to 68 keV than 77 keV if the above-mentioned conversion and fluorescent figures are correct. No accurate study of this point has been attempted since a comparison is always made with a mercury standard. In this connexion, it should be remarked that in this paper we often speak of "the 77 keV peak of Hg^{197}" where one properly should say "the 77 keV plus the 68 keV peaks together".

The alternative to the scintillation detector at present seems to be the Xe-filled proportional detector, especially in the form developed by PEIRSON at the Atomic Energy Research Establishment.[16] With it, one would expect two to three times narrower peaks, i.e. the background can be suppressed, the disadvantage being a relatively low efficiency. (It is planned to compare this detector with the NaI detector later on).

The pulse spectra from the NaI-detector were fed to a single-channel analyser (designed by K. Ljunggren). This unit has the advantage, amongst others, that a preselected part of the spectrum can be chosen and that marked pulses are given at regular intervals, thus facilitating calibration. Recently, a multi-channel analyser (Hutchinson–Scarrott type modified by M. Setterwall and manufactured by Sivers Lab, Hägersten, Stockholm) was available and has been used successfully in many cases.

Further details are given in the Section *Procedure Adopted*.

EVAPORATION PRECAUTIONS

Before the method itself is discussed, the difficulty of evaporation has to be considered since it is one of the most important points in this method.

It has been found that, even at moderate temperatures, mercury disappears from samples of various kinds during irradiation in the reactor.

This was first observed as irregular experimental figures for known mercury contents.

The evaporation processes have been studied using the long-lived isotope Hg^{203}. Solutions of Hg^{203} in the form of $HgCl_2$, cyano-methyl-Hg-guanidine and C_6H_5 HgAc were prepared. The concentrations were about 100 μg Hg/ml.

Small amounts (about 0·05 ml) of these solutions were taken by pipette and placed on strips of cellulose (about 4 cm^2) comprising about 200 mg material. The water was then evaporated very carefully. In some cases, hydrogen sulphide was applied before drying. The samples were then counted in a well-type scintillation counter in order to establish the starting values. Thereafter, the samples were kept at 105°C in air. The γ-activity was controlled at intervals. The results can be readily seen in Fig. 4. It is

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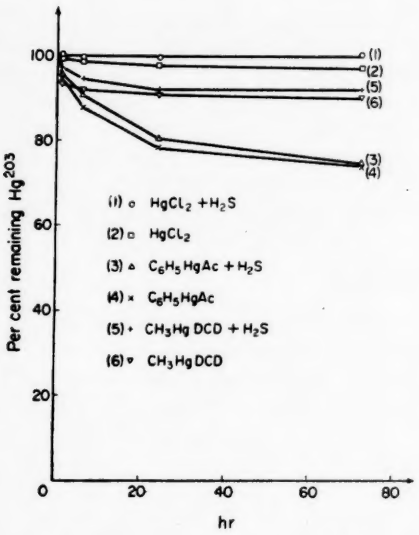

FIG. 4. Evaporation of mercury from cellulose samples at 80°C. CH_3HgDCD = cyano-methyl-Hg-guanidine. Hg^{203} was used. A special sample which was kept at room temperature was followed in order to correct for decay and changes in the counting apparatus. All initial activities of the six samples have been normalized to 100 at the beginning of heating. The initial activities were of the order of 13–28000 c.p.m. All samples were counted for 5 min.

seen that the samples treated with H_2S exhibit a smaller evaporation rate. We also see that the metal–organic mercury compounds show the same order of volatility under these conditions. They are less affected by H_2S, presumably due to the non-ionic structure of these molecules which may prevent any HgS being formed.

It was thought that careful wrapping of the samples in aluminium foils would prevent the escape of mercury during reactor irradiation. Laboratory experiments using Hg^{203} as well as reactor activation (Hg^{197}) showed that this is not the case, which is a little surprising. We did not pursue the investigation of this question further. It is only necessary to remark here that not only evaporation should be considered but also the formation of metallic mercury vapour according to the findings of FREYSCHUSS *et al.*[17].

Another study of the evaporation was made in a more step-wise fashion and is shown in Fig. 5. The samples were prepared in the same way as before (Fig. 4). These studies show that evaporation is still measurable at 50°C for the metal organic compounds but not for $HgCl_2$.

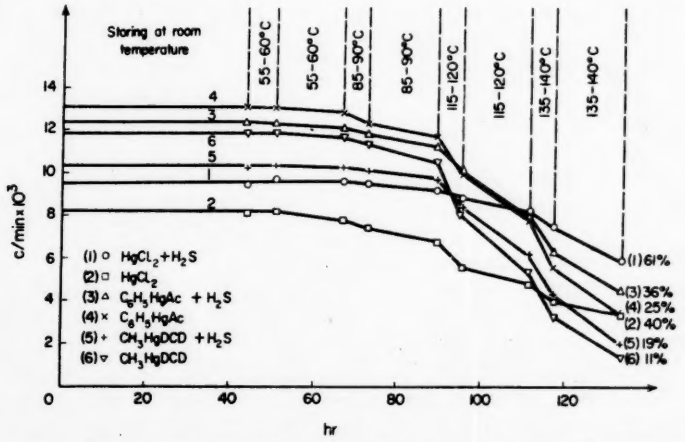

FIG. 5. Evaporation of mercury from cellulose samples. Known volumes of solutions containing mercury in different chemical forms (see figure) were dropped on to cellulose samples. A special sample (which was never heated) was used to correct for decay and changes in counting efficiency. Counting was made in a NaI(Tl) well-type scintillation detector, 5 min for each sample. The samples were kept at a certain temperature for the time indicated. CH_3HgDCD = cyano-methyl-Hg-guanidine. It is evident that evaporation is serious even at 50–60°C and even if H_2S treatment is used. At the right-hand end of the figure, the per cent Hg remaining after the whole of the procedure is given.

The actual temperature in the R1 reactor is not accurately known. The D_2O moderator is at present kept at 35°C but, during an earlier period, about 50°C was held. The absorption of γ-radiation and fast neutrons as well as neutron capture should give some additional measure in temperature which is very dependent on the insulating properties of the samples and their geometry. This point has not been studied in detail but, from the evaporation data, we have learned that it is high enough to cause serious losses.

We therefore had to conclude that no samples, where mercury is of interest, can be kept without complete sealing.

METHODOLOGICAL TESTS

Since it was evident (see preceding section) that evaporation is a deciding factor in our method, all experiments except the test to be described below were performed using sealed quartz glass tubes.

Reactor irradiation was performed for 2–3 days and, thereafter, aging for 2–3 days. These conditions optimize the activity. It is a very fortunate circumstance that, after this time, the sample can be studied spectrometrically without opening the tube. The quartz showed some activity after irradiation, first of all from Si^{31} (2·6 hr) but also from Na^{24} and As^{76} (arsenic seems to be present in some parts per million in the quartz glass used here). The gamma radiation of Hg^{197} is attenuated to about 95 per cent in the 0·5–1 mm quartz glass and the absorption in the sample itself is of the same order. The variation from tube to tube should therefore not introduce a larger error than 2 or 3 per cent.

If evaporation of mercury takes place within the tube, or metallic mercury has been formed in connexion with the heating in the reactor, this does not disturb the measurements at all.

A typical Hg^{197} spectrum is shown in Fig. 6 in which a representation of the background is suggested. In almost all cases encountered, the Hg^{197} gamma peak stands on a rather low background. This is a fortunate case in this type of activation analysis and it renders possible a rather good sensitivity.

The method has been tested by means of the analysis of known amounts of mercury. This was performed in the following way. Known volumes (with an Agla microsyringe) of a $HgCl_2$ solution were placed on cellulose samples. The volumes were varied in exact whole number proportions from 1 to 10. Each "unit" comprised about 3 μg. The samples were then treated with a H_2S solution.

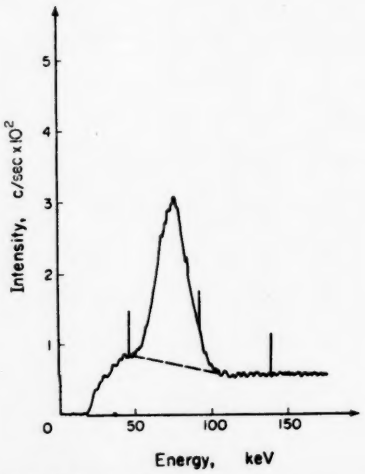

FIG. 6. Record of Hg^{197} gamma spectrum in the region 0–150 keV present in a piece of liver of a rabbit exposed to mercury vapour (from the VESTERBERG–TEJNING project, cf. text). The suggested background drawing has proved practical although it does not include the escape peak.

The drying was performed very gently and the samples were then wrapped in individual aluminium packages and put in a standard aluminium can ($\phi = 25$ mm), irradiated, aged and, after rewrapping in inactive aluminium, studied spectrometrically.

The experimental material lends itself to a statistical "straight line test". Such tests of activation analytical methods have been made by LEDDICOTTE[18] using the procedure by YOUDEN[19]. Using the symbols and the procedure of YOUDEN, we find by analysing

the data of Table 2 that the slope is 0·985, i.e. close to one. It should be remarked that one point, No. 10, is used to normalize the material. The *t*-test shows that the slope is not systematically different from one. The intercept is 0·03 but it is also insignificant.

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TABLE 2

Relative amount	Test of accuracy*		Average value	Amount† found	Deviation
	$Area_1$	$Area_2$			
10	35·2 35·1	35·0 34·7	35·0	10·0	± 0%
9	31·9 30·3	31·5 30·4	31·0	8·86	−1·5%
8	28·0 27·6	27·7 28·1	27·85	7·96	−0·5%
7	23·9 23·2	23·5 23·3	23·5	6·72	− 4%
6	20·2 20·2	20·0 20·4	20·3	5·77	−3·8%
5	18·5 18·2	18·2 17·9	18·15	5·22	+4·4%
4	13·9 13·4	13·9 13·3	13·35	3·88	− 3%
3	10·4 10·5	10·1 10·5	10·4	2·95	−1·7%
2	7·2 7·2	7·0 7·3	7·2	2·06	+ 3%
1	3·7 3·6	3·5 3·6	3·6	1·03	+ 3%

* Spectra have been recorded twice, once with increasing and once with decreasing energy. $Area_1$ and $Area_2$ refer to these two cases. In each case, two planimeter readings were taken to avoid personal errors.

† Normalized to the sample No. 10.

If we assume that the line goes through the origin, the slope is also insignificantly differing from one. Thus the 45° line test shows that the method is very reliable. The deviations recorded in Table 2 never exceed 5 per cent. The standard deviation of single points is about 3 per cent. It should be remarked that this investigation was made possible by the non-volatility of the H_2S-treated $HgCl_2$ cellulose. It would, of course, have been impossible for the metal organic mercury compounds. The result of the investigation is very satisfying and should be applicable, on the whole, to the case where quartz tubes are used.

Fig. 7 shows the results graphically.

The conclusion can be drawn that, provided background conditions are not worse than in these cases, mercury in amounts ranging from 3 to 30 μg can be measured with a precision corresponding to not more than about a 5 per cent deviation from the "true" value. It can also be concluded from these results that, apparently, no trouble has been caused by epithermal resonant neutron capture (cf. the above section *Neutron Irradiation*).

From the data obtained and general experience, it can be inferred that the present sensitivity limit is about 0·03 γ,

i.e. 0·03 p.p.m. if 1 g samples are used. It should be stressed that this applies to conditions where the ratio of gamma peak to background is of the same magnitude as in the samples studied (for exceptions see below).

PROCEDURE ADOPTED

Our experience concerning activation of mercury can be summarized in the following recommended procedure which may be considered as a normal case.

Weigh out 0·1–1 g (normal case 0·3 g) of a sample which has not been heated. Seal it in a quartz tube of about 8 mm diameter and 60 mm length.

The standard is prepared in the following way: take a known amount (of the order of 0·01–0·1 ml) of a freshly prepared solution of $HgCl_2$ on a filter paper. Add about the same volume of a saturated H_2S solution. Evaporate carefully to dryness. Seal as above for the sample (cf. practical note below). Place sample and standard close together in the irradiation can (several samples and standards may be put in the same can) and irradiate for 2–3 days at 5–10 $\times$ 10^{11} n/cm^2 sec thermal. Take out can and age for at least 2 days.

Place individual (now violet) quartz tube in a suitable measuring position with respect to the NaI detector. Record spectra at least twice. Record spectrum of the standard within a few hours by using the same measuring conditions. Repeat recordings the following day. Estimate background. Measure planimetrically areas of sample and standard. Break tube, heat and find water content if necessary. Correct Hg content to dry sample. Calculate amount. Use the second day's data to ensure that Pt^{197} is not present. If the apparent Hg content has changed, follow it more carefully and calculate Hg and Pt contents separateiy. The latter determination is rougher if relative cross-section data are used instead of a good Pt standard.

COMMENTS AND DISCUSSION

The total error of the procedure is composed of the following parts (negligible means less than 0·1 per cent),

- weighing errors (negligible)
- volumetric errors (also negligible)
- differences in wall thickness of quartz tubes (about 2 per cent at most)
- flux depression (maximum 1 per cent)
- neutron self shielding (maximum 0·3 per cent, difficult to estimate resonance neutrons)
- flux topography (maximum 1 per cent)
- recording of spectra (instrumental reproducibility 1–2 per cent)
- planimetry (negligible)
- background drawing (important, depends much on type of sample and mercury level; may be the deciding error).

The way of performing the background drawing can be discussed extensively. We shall only note here that the "bump" due to *K*-escape of the 68–77 keV peak should be treated in the same manner for sample and standard (cf. Fig. 3). The dotted background drawing suggested in Fig. 3 has been used in most cases. Even if it can be objected that a more symmetrical drawing is fundamentally more correct, our way of drawing is practical, however, and does not seem to introduce any considerable error. This is confirmed from the straight line test (cf. Fig. 7 and text) where the method was used.

The resulting maximum error cannot be assessed with any certainty. The results used for the straight line test (Fig. 7) include many of the errors mentioned here except for part of the background error and, moreover, the flux depression is less than in the quartz tube case and the result there should give a good idea of the errors in unknown samples provided the signal size and signal/background are comparable. Thus our experience is that the total error of single determinations does not exceed 5–10 per cent (95 per cent confidence level). A better accuracy is seldom required in trace analyses. The case

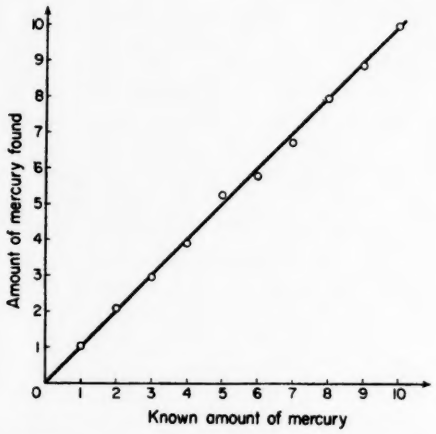

FIG. 7. Straight line test of Hg activation analysis. The line is drawn through the origin and through the point (10·0, 10·0) which served as a standard in this experiment. Table 2 shows the deviations between found and "true" figures. One unit of the *x*-axis corresponds to about 3·0 μg Hg.

of seed treatment mentioned below constitutes an exception. A greater precision was required for the seed treatment investigation and was, in fact, obtained because it involved comparative measurements. In no case have we detected Pt^{197}. The time required for six samples and two standards is about 2 hr before reactor irradiation and 5 hr for the spectrometry and treatment of the results.

If lower contents are present, we gain very little by taking larger samples because the background also increases. The case of blood mentioned below was very close to our present detection limit. The use of a multichannel analyser was tried and a longer aging but, due to the background, no better results than with the single-channel analyser were obtained.

All these results apply to a flux not larger than 10^{12} n/cm^2 sec. The advent of high flux reactors (order of 10^{14} n/cm^2 sec) can reduce the sample size by a factor of 100, i.e. biological milligram samples can be studied. On the other hand, when using normal samples, one should be able to age further and thus gain in sensitivity how much can only be found experimentally since longer-lived activities may set a limit (P^{32}, Fe^{59}, Zn^{65}, etc.).

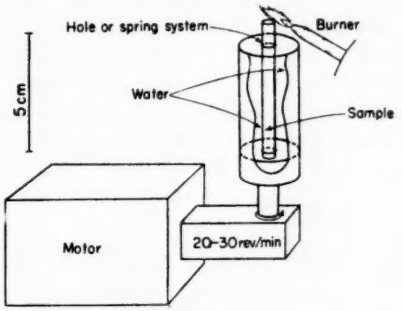

FIG. 8. Sketch illustrating the quartz tube sealing technique.

Partial heating of the quartz tubes and trapping of the mercury in a cold part of the tube (perhaps on gold metal) may be selective enough to permit a large increase in the sensitivity. In such a case, special experiments would have to be performed to ensure that all of the mercury had been evaporated. We have, however, not yet made any studies of this type.

APPLICATIONS

Biological tissue and other biological and organic materials

The method has been applied to a large number of samples from an extended investigation by VESTERBERG and TEJNING[20], concerning the toxicology of mercury, and samples from other investigations including various organic materials (e.g., pharmaceuticals). The samples analysed have comprised human faeces and hair; brain, liver, kidney, glands, muscle, blood, etc., from rabbits and chickens. Usually, 0·3 g of these substances have been used. They were all treated as described above. Radiation chemical changes were always observed but this is of no concern in the method. Typical values obtained were 2–20 p.p.m. The lowest amount was 0·3 (blood) and the highest 150 p.p.m. In many cases, the results have been compared with those

obtained with a spectrophotometric procedure by VESTERBERG and SJÖHOLM[25]. The agreement was good.

Blood samples were analysed in a few cases. In one case, the spectra showed a small peak at the right place (68–77 keV) and the quotient relative to a standard was constant during 3 days of observations. The content was only 0·3 p.p.m. (0·5 g samples were used). This is near the limit of detection and the data are therefore uncertain in this region. It is only the combined support of the correct peak energy and the correct half-life which makes a conclusion possible. This example is of course not representative. Newer analyses of blood with higher concentrations of mercury have met with no difficulties and good results have been produced.

It has been noted that *bone* is not particularly suitable for this spectrometric method. There is produced a continuous gamma spectrum most probably due to bremsstrahlung from P^{32} which is formed in the bone phosphorus by $P^{31}(n,\gamma)P^{32}$ and by $S^{32}(n,p)P^{32}$. The limits of detection have not been elucidated. It can be said, however, that mercury contents of the order of 1–5 p.p.m. are definitely difficult to detect. In the case of bone (and teeth), some chemical or mechanical (distillation) separation should be considered.

PULP AND PAPER

The method has been applied to cellulose and mechanical pulp with great success. Where possible, the results have been checked against other methods, notably the gas spectrophotometric method.[21] The details will be described in a special publication.[5]

SEED SAMPLES

The problem was put forward by LINDSTRÖM. Seeds which have been subjected to liquid seed treatment contain minute amounts of organic mercury. The Hg distribution produced by commercial treatment was to be determined by the mercury analysis of individual kernels of treated seed and the data thus obtained subjected to a statistical treatment.

TABLE 3. Mercury analyses in individual kernels of treated seed. (Wheat seeds treated with Panogen 4925 containing 0·8 per cent Hg as cyano(methylmercury) guanidine. The treatment was performed at the Östgöta Lantmännens Centralförening, Norrköping, using the Panogen Seed Treater, Model JS)

Sample No.	Amount (γ)	Mass of grain (mg)	Hg (p.p.m.)
1	0·69	47·1	14·7
2	0·74	37·1	20·0
3	0·75	42·7	17·6
4	0·86	57·8	14·9
5	0·62	36·5	17·0
6	0·53	34·9	15·2
7	0·75	52·3	14·4
8	0·68	51·9	13·1
9	0·76	44·1	17·2
10	0·66	35·7	18·5
11	0·75	48·8	15·4
12	0·74	34·6	21·4
13	0·72	45·4	15·8
14	0·72	40·0	18·0
15	0·71	46·5	15·3
16	0·65	41·4	15·7
17	0·64	28·9	22·1
18	0·54	28·3	19·1

TABLE 4. Tests of three different analytical methods for Hg on some treated seed grains

Seed No.	Activation analysis	Hg according to	
		Tracer method (μg)	Gas spectrophotometric method (μg)
1	0·79	0·75	0·77
2	0·52	0·46	0·49
3	0·59	0·60	0·68
4	0·53	0·45	0·42
5	0·74	0·79	0·80

Each grain, weighing only about 40 mg, was quartz-sealed individually and the procedure described above applied. No difficulties in finding the peak was found. Table 3 contains typical results for the measurements.

From the deviations from the average, variance coefficients were calculated which yielded information concerning the result of the liquid seed treatment process.[21,22]

Some tests were made on the same individual seed grains using different methods of analysis. Table 4 indicates that the figures obtained using activation analysis and a tracer method employing Hg^{203} at a known specific activity (measured with a well-type NaI-crystal) and the gas spectrophotometric method[21,22] agree. It should be remarked that the small amount of Hg^{203} did not disturb the activation analytical procedure—a very fortunate circumstance.

These methods and the results in Table 4 are due to LINDSTRÖM and are published with his permission.

ALUMINIUM AND CORRODED ALUMINIUM PRODUCTS

Samples of aluminium and its corrosion products (white oxidized products mixed with metal) from a paper factory were sent for mercury analysis.

Our routine procedure was followed and extremely well-recorded mercury peaks were obtained. The contents ranged from 10–50 p.p.m. suggesting that mercury had played a part in the corrosion process. Ordinary laboratory methods for mercury in this case were stated to be too insensitive. We may conclude that aluminium products of this kind are a very favourable case for our method. It may, in addition, be possible to study lead and also other less easily neutron activated substances.

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HISTORICAL REMAINS

There is an unsolved problem in Swedish history concerning the death of King Erik XIV. Some writers claim that the King was poisoned by his brother but other authors disagree. Parts of the remains of the King were available in 1958 and, as mercury and arsenic were among the poisons possible, we were requested to apply our activation analytical method for mercury to these samples. Some low mercury values were obtained. The results will be given in a special publication.[23] In this connexion, we worked out an identification test using the combined evidence from gamma energy and half-life. This method is also reported separately.[24] It should be noted that, in that report, Hg^{197} in these historical remains is taken as a proof of identification.

EARLIER PRESENTATION

A note on the method was presented orally as a discussion note in the analytical section of UNESCOs Isotope Conference in Paris, 1957, but was not included in the proceedings. It has been reported in a lecture before the Analytical Section of the Swedish Chemical Society on December 3 1957 and in the Analytical Conference on May 29 1958 in Lund. Its further extension was reported before the Swedish Society for Medical Physics and Techniques, October 24 1958. At the Vienna Symposium on Activation Analysis, June 3 1959, K. Ljunggren of this Institute presented a report on this work which will be included in the Proceedings of that Symposium. The present paper includes all improvements made during the time indicated.

Acknowledgements—This work was made possible by a number of sponsors, especially the Casco Company. Dr. O. LINDSTRÖM of this company has contributed with valuable discussions and encouragement. He has also kindly put the Hg^{203} solutions at our disposal.

Drs. VESTERBERG and TEJNING have given us valuable support and economic assistance. Several comparisons with their analytical results have been made. Dr. VESTERBERG has kindly read parts of this manuscript and suggested certain changes which were subsequently made.

As was stated above, the studies of cellulose material will be reported separately together with Dr. P. O. BETHGE of the Swedish Forest Products Research Laboratory. Dr. BETHGE has, however, given us constructive criticism of the work described above.

Thanks are due to Holmens Bruks och Fabriks AB Hallstavik, for their permission to report the note on aluminium corrosion.

The co-operation of Mr. C. G. Österlundh, Dr. E. Haeffner and Mr. T. Petersén of the AB Atomenergi is gratefully acknowledged. They have not only performed all irradiations but also furnished data on flux topography, temperatures, etc.

The instruments used have been designed, constructed and maintained by K. Ljunggren and have been procured through the economic support of the Swedish Atomic Committee and the Council of Technical Research.

The authors also wish to thank the Head of the Institution, Professor Ole Lamm, for continuous support and excellent working conditions.

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PRACTICAL NOTE

Since the sealing in quartz tubes in the case of mercury-containing materials may not be trivial, our method for this will be described shortly.

The tubes used were made from ordinary quartz glass tube, available here in 0·5 m lengths. The tubes were cut to about 60 mm, sealed at one end and carefully cleaned (chromic acid, distilled water, alcohol, annealing) before inserting and weighing the samples. The tube length, of course, depends on the size of the irradiation can used but should be at least 40 mm to ensure that no radiant heat damage of the sample occurs during the sealing process. For the same reason, samples should be placed only in the lower part of the tube. The sealing was made under water cooling of the tube's sample region (Fig. 8) by means of some kind of high temperature burner (>1700°C). Up to now, we have used an ordinary welding burner (acetylene–oxygen) for this purpose but a hydrogen–oxygen burner might be still more effective. The sealing must be done rapidly (in a few seconds) to prevent heat from spreading to the tube's sample region.

The apparatus shown in Fig. 8 has been used for sealing several hundreds of samples without any indication of serious heating effects. The apparatus consists in its simplest form of a small water-filled can with a hole in the cover fitting the tube or, still better, some kind of spring system fitting a certain range of tube diameters to keep the tube in the centre of the can. The can is mounted vertically and rotated slowly (20–30 r.p.m.) around its axis by means of a small motor. The tube is inserted in the can ($\frac{4}{5}$ of the tube under water) and is then ready for sealing. The water should be changed frequently when sealing a number of tubes in series.

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A Graphical Determination of Uranium and Thorium in Ores from Their Gamma-ray Spectra

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(*Received* 2 *February* 1960)

A graphical method is described for calculating the uranium and thorium contents of ores. The intersection of straight lines, each relating to a selected interval in the gamma-ray spectrum, makes possible a rapid estimate of the respective contribution of each series (uranium and thorium) to the total gamma activity. The departure from equilibrium in the uranium series and the effect of potassium are both considered. Spectrum curves were plotted for crushed ore samples. Count yields in a number of selected spectral intervals are given for natural uranium, natural thorium, purified uranium oxide (less radium and daughters) and potassium, to illustrate the construction of the linear equations. Typical solutions are shown for several types of ore samples.

SOLUTION GRAPHIQUE DES SPECTRES DES RAYONS GAMMA ÉMIS PAR DES MINÉRAIS POUR LA DÉTERMINATION DE L'URANIUM ET DU THORIUM

La présente étude décrit une méthode graphique de calculer la teneur des minerais en uranium et en thorium. L'intersection de lignes droites, dont chacune se rapporte à un intervalle choisi du spectre de rayons gamma, permet de calculer rapidement la contribution respective de chaque série (uranium et thorium) à l'activité totale des rayons gamma. On tient compte du déséquilibre dans la série de l'uranium et de l'influence du potassium. Les courbes spectrales ont été tracées dans le cas d'échantillons de minerai broyé. On donne les relevés numériques dans un certain nombre d'intervalles spectraux choisis dans le cas de l'uranium naturel, du thorium naturel, de l'oxyde d'uranium purifié (moins le radium et les produits de filiation) et du potassium, en vue d'expliquer la construction des équations linéaires. On montre des solutions caractéristiques de plusieurs types d'échantillons de minerai.

ГРАФИЧЕСКОЕ ОПРЕДЕЛЕНИЕ УРАНА И ТОРИЯ В РУДАХ ПО ИХ ГАММА-СПЕКТРАМ

Описан графический метод расчета содержания урана и тория в рудах. Пересечение прямых линий, каждая из которых соответствует заданной области гамма-спектра, дает возможность быстро определить долю активности каждого члена (урана и тория) в общей гамма-активности. Рассмотрено отклонение от равновесия в ряду урана, а также влияние калия. Кривые были построены для размельченных образцов руды. Чтобы показать характер линейных уравнений, приводится число импульсов счетчика в определенных областях спектра гамма-излучения природного урана, пророднего тория, очищенной окиси урана (без радия и дочерних соединений) и калия. Даны типичные примеры решения задачи для нескольких видов руды.

GRAPHISCHE BESTIMMUNG VON URAN UND THORIUM IN ERZEN AUS IHREN γ-STRAHLSPEKTREN

Es wird eine graphische Methode beschrieben zur Errechnung des Uran—und Thoriumgehaltes von Erzen. Der Schnittpunkt gerader Linien, deren jede sich auf ein ausgewähltes

Intervall im γ-Strahlenspektrum bezieht, erlaubt eine rasche Abschätzung des relativen Beitrages jeder Zerfallreihe (Uran und Thorium) zur gesamten γ-Aktivität. Sowohl die Abweichung vom Gleichgewicht in der Uranreihe als auch der Einfluss des Kalium werden berücksichtigt. Es werden Spektren zerkleinerter Erzproben dargestellt. Um die bildung der linearen Gleichungen klarzumachen, werden Zählergebnisse von einer Zahl ausgewählter spektraler Intervalle bei naturlichem Uran, natürlichem Thorium, gereinigtem Uranoxyd (weniger Radium und Tochterprodukte) und Kalium angegeben. Typische Lösungen für verschiedene Arten von Erzproben werden gezeigt.

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INTRODUCTION

THE early radiometric methods of determining the uranium content of ores depended merely upon a measurement of total activity. This was an oversimplification and could lead to serious errors when thorium was present, or when the decay products of uranium, themselves important contributors to the total activity, were not present in their usual proportions (i.e. the uranium ore was "out of equilibrium"). Extreme departures from the equilibrium condition were found in some mill samples as a result of leaching and other chemical processes. However, leaching may also have occurred in nature and led to the formation of secondary minerals. Thus, an excess of uranium relative to the radium daughters could result in some areas, and there might be a deficiency in others.

The development of the "equilibrium method" enabled these problems to be solved if they were encountered separately. This method, based on the solution of simultaneous equations derived from separate beta and gamma determinations, was outlined by LAPOINTE and WILLIAMSON[1] and, independently, by THOMMERET[2]. Its widespread adoption awaited the development of more sensitive detectors: a counter with adequate sensitivity for this purpose has been described by EICHHOLZ *et al.*[3].

The method is useful for most types of radioactive ore encountered; however, only two sources of activity can be separated from a combination when as many as four independent natural groups of radioactive elements might in fact occur together. As an improvement of that method, operation of the gamma scintillation counter at two or three different gain settings will provide additional information through "energy discrimination". However, with the advent of the scintillation spectrometer it has become more convenient to examine simultaneously a number of separate energy bands, or peaks, in the gamma-ray spectrum.[4]

In this way, the separate contributions to the total count from individual emitters, or from groups of emitters, may be found for each of several spectrum regions from standard calibration samples, and may be expressed as the count rate per gram of the oxide within the spectrum region specified, while using a particular sample geometry. In a sample containing a combination of gamma-ray emitters the count rate in a given region, or energy interval, may be expressed as a linear equation

$$C = au + bt + ck + \ldots$$

where a, b and c are constants determined from standard samples. These constants will have various values throughout the spectrum, becoming zero above the highest energy emitted. u, t and k are the weights of the oxides to be calculated.

By a choice of spectrum intervals the equations for the unknowns u, t and k may be solved two at a time, working down the spectrum toward the lower energy levels of radiation.

A number of equations of the form

$$C_1 = a_1u + b_1t$$
$$C_2 = a_2u + b_2t$$
$$C_3 = a_3u + b_3t$$
$$C_4 = \text{etc.},$$

may be conveniently solved using intersecting straight lines in a graphical Cartesian system. From the straight lines (five being a

convenient number) which intersect in practice in a small area, the best solution may be found by inspection, rapidly and with an accuracy comparable with the rest of the procedure. The failure of a line to pass through this small area may have some significance, as will be shown later in the examples.

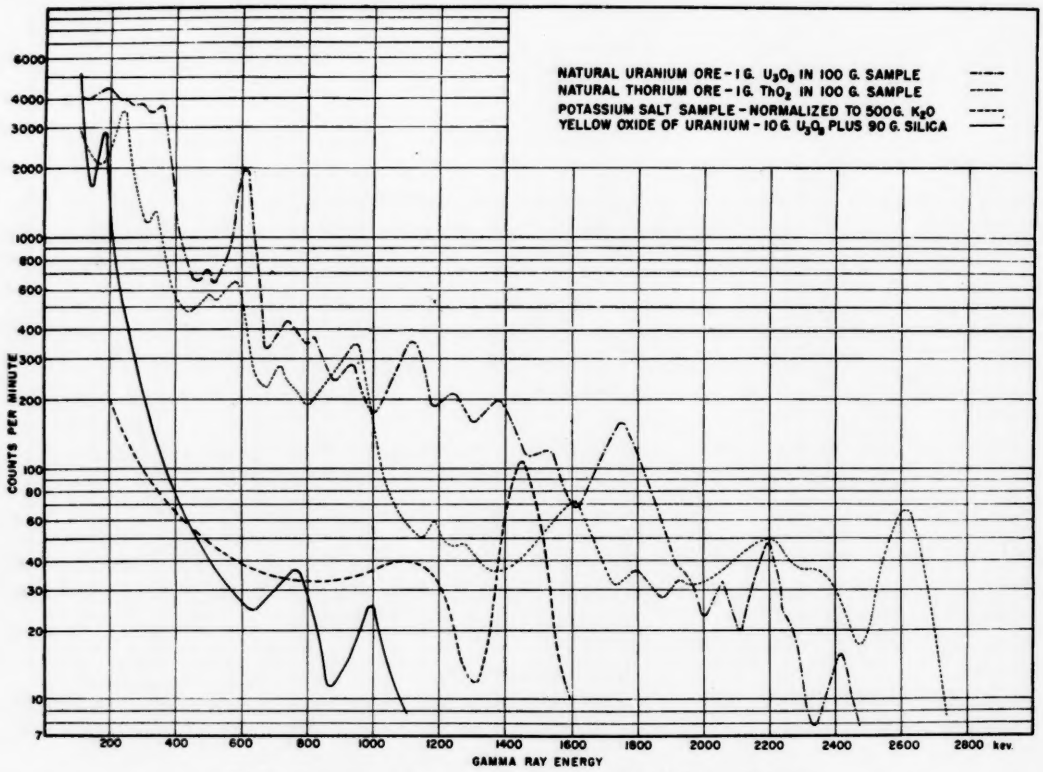

FIG. 2. Gamma-ray spectra from natural ores or their constituents.

DESCRIPTION OF THE METHOD

In the spectrometer shown in Fig. 1, a cylindrical sodium iodide crystal, 5 cm thick by 5 cm in diameter, was mounted on an RCA type 6655 photomultiplier tube as the radiation detector. The pulses from the tube are amplified, shaped and fed to a multi-channel analyzer.*

The crystal was mounted with particular attention to factors affecting resolution and the transmission of low energy gamma rays. The photomultiplier tube was carefully selected for minimum drift with change in count rate.[5] The customary method of calibration was employed, using radioisotopes of known energy levels, such as Co^{57}, Cs^{137}, Zn^{65} and Co^{60}. Spectra obtained from natural uranium ore, purified uranium oxide (radium and its daughter elements removed by purification), natural thorium, and potassium are shown in Fig. 2.

As is evident from the figure, the gamma-ray spectra of the uranium and thorium series are very complex, with many overlapping peaks. While the thorium series can best be distinguished from the uranium series by measuring the 2·62 MeV gamma

* The five-channel Marconi pulse-height analyzer (Model CMC 115-935; AEP 516) used for most of this work was replaced in later work by a 100 channel transistorized analyzer (CDC Model AEP-2230).

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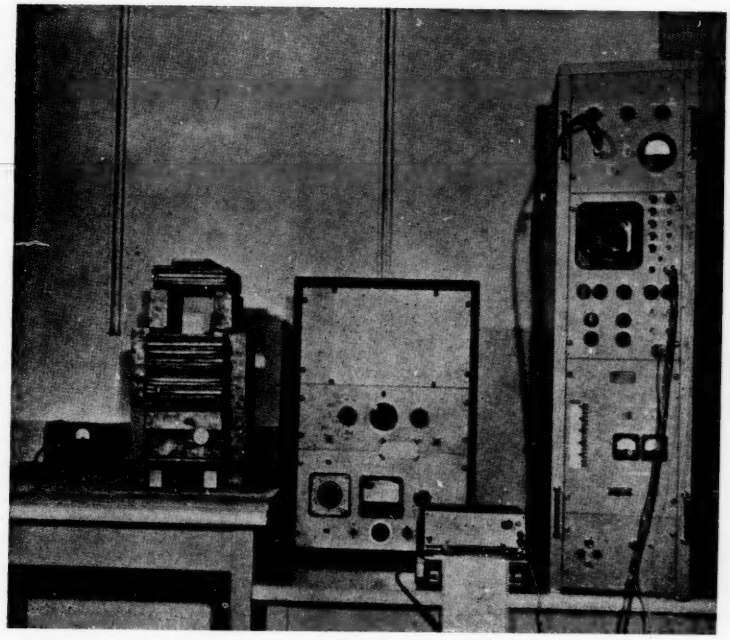

FIG. 1. View of gamma-ray spectrometer.

TABLE 1. Count yields in selected spectral intervals from natural emitter groups

Energy range (keV)	Counts per minute per gram				Background (c.p.m.)
	U_3O_8 (natural)	U_3O_8 (purified)	ThO_2 (natural)	K_2O	
20–40	2400	380	1015	0·21	5
40–60	4210	1090	1680	0·33	11
60–80	7140	1700	3350	0·31	17
80–100	4080	1850	2160	0·15	8
100–200	10400	1540	5790	0·44	22
200–300	9300	486	6580	0·55	19
300–400	7720	166	2440	0·36	26
400–500	1880	62	1270	0·26	18
500–600	2320	44	1450	0·20	10
600–700	2280	34	738	0·19	11
700–900	1720	55	1146	0·35	18
900–1100	1190	53	993	0·42	13
1100–1300	1170	6	254	0·36	9·4
1300–1500	772	2	198	0·59	7·3
1500–1700	460		288	0·096	6·6
1700–1900	552		161		2·6
1900–2100	152		171		1·8
2100–2300	150		219		2·3
2300–2500	51		140		1·8
2500–2700	(9)		220		1·5
over 2700			28		28·4

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ray from its daughter element Tl^{208}, so few counts are available from a low-grade sample in this region of the spectrum that additional information must be sought at lower energies where pronounced thorium peaks occur. Uranium and its immediate decay products, in contrast with those following radium, can only be measured with any degree of sensitivity in the low energy region below 0·1 MeV. Potassium, which is weakly radioactive in nature, can be measured by means of its radioactive isotope K^{40} using a narrow spectral region around 1·46 MeV, provided that other sources of activity are low. Conversely, because of its low specific activity, potassium is not usually a serious source of error in thorium and uranium determinations in other regions of the spectrum. Table 1 shows the count yield at a number of intervals of the gamma-ray spectrum, obtained from standard samples with the particular sample geometry used with this detector. The sample containers were glass jars having an internal diameter of 4·5 cm. Generally, a 100 g sample was used and the sample thickness was then 5 cm; an empirical correction curve was determined for other sample weights and thicknesses. The curve shows that a very precise determination of sample weight or thickness for a 90–110 g sample is not necessary, since the major contribution to the total count rate originates in the 30 g fraction closest to the detector; on the other hand, it does indicate the importance of careful sample mixing and the prevention of segregation. This correction curve is not applied below 200 keV, because the effect of self-absorption in the sample becomes increasingly important as the energy decreases.

CALCULATED EXAMPLES

The count yields from the standard samples in Table 1 were combined mathematically to produce a range of imaginary examples to illustrate the use of the graphical method of solution and the required counting time for a given ore grade and composition,

TABLE 2. Calculated examples (based on Table 1) 10 min count yield

Channel number	Energy range (keV)	U_3O_8 (purified) (0·1 g) O	U_3O_8 (natural) (0·1 g) U	ThO_2 (natural) (0·1 g) T	K_2O (30 g) K	No. 1 U + T	No. 2 O + U	No. 3 O + U + T	No. 4 U + K	No. 5 U + T + K
1	40–60	1090	4210	1680	99		5300	6980		
2	60–80	1700	7140	3350	93		8840			
3	80–100	1850	4080	2160	45		5930	8090		
4	100–300	2026	19700	12370	297	32000			20000	
5	300–500	228	9600	3710	186	13300				13500
6	500–700	78	4600	2190	117				4720	
7	700–900	55	1720	1146	105					
8	900–1100	53	1190	993	126				1320	2309
9	1100–1300	6	1170	254	108					
10	1300–1500	2	772	198	177	970		972	949	1147
11	1500–1900		1012	449	29		1012			
12	1900–2300		302	390		692			302	
13	2300–2500		51	140				191		191
14	2500–2700		(9)	220		229		229		229

Note: Weights indicate amount of oxide per 100 g sample.

ignoring possible effects of drift and statistical fluctuation. These examples are presented in Table 2, and the graphical solutions are shown in Figs. 3–7. A sample calculation is given in the Appendix.

Consider the previous equation, $C = au + bt$, representing the count in any spectral region resulting from two groups of radiation emitters, natural U_3O_8 and ThO_2 for example, whose weights (as the oxides) are u and t g. A line is plotted for this equation by the intercept method, which amounts to considering the count C first to be due solely to uranium, and then solely to thorium. Points intermediate to the intercept points represent various proportions of uranium and thorium which could give the same count rate C. A similar line, having a different slope, can be obtained in another spectrum interval, if the relative sensitivity to uranium and thorium (a/b) is different. The intersection of the two lines will occur at the point representing the actual weights of u and t in that sample. In practice it is advantageous to establish the point (or small area) of intersection by means of additional lines from a total of five to ten channels—the number being limited to minimize calculation. It is evident that the spectral regions should be chosen to provide a range of lines with widely differing slopes, to render more definite the area of intersection.

The count rates in the examples shown are those which would be obtained during a 10 min period. Fig. 3 illustrates a 100 g sample containing 0·1 per cent U_3O_8 and 0·1 per cent ThO_2; i.e. u and t each equal 0·1 g. Note that L_5, representing the channel of highest energy, is almost parallel to the uranium (+radium) axis; this channel, number 14, is almost entirely above the highest energy peak emitted from the uranium series.

In the next example (Fig. 4) there are equal quantities of natural uranium ore and purified uranium oxide. In this case L_4 is parallel with the axis representing the weight of the purified uranium oxide for the same reason as in the previous example. The oxide used for this work was several months old, having reached equilibrium in so far as the short-lived daughters were concerned. The results would not apply to freshly prepared mill samples, but serve to show how departure from equilibrium in the uranium series can be determined. The contribution from the purified oxide (less the radium daughters) can be made to exceed 40 per cent of the count obtained from natural uranium in a narrow region of the spectrum near 80 keV; however, the use of a narrow

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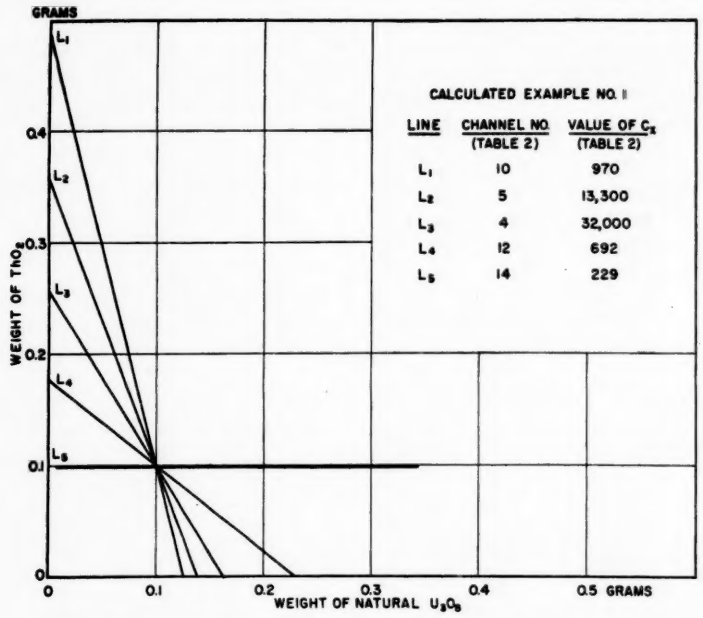

FIG. 3. Theoretical example for a mixture of ThO_2 and natural U_3O_8.

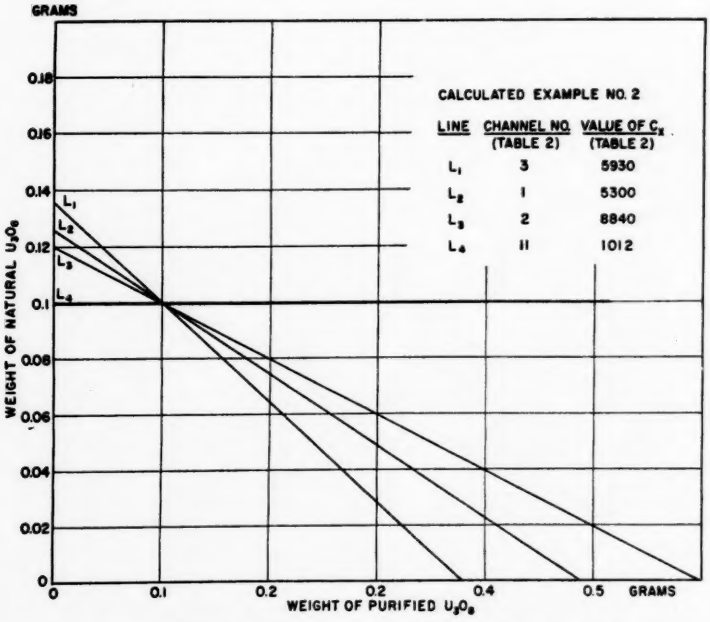

FIG. 4. Theoretical example for natural and purified U_3O_8.

channel requires correspondingly better stability.

In Fig. 5, a solution is obtained for natural U_3O_8 and ThO_2, considering both to be in equilibrium with their daughters. Since this fictitious sample contains, in addition, purified uranium oxide (equal in weight to the U_3O_8), the lines L_2 and L_3, representing the synthetic ore sample (No. 4/59-K) containing 10 per cent K_2O, 0·05 per cent ThO_2 and 0·05 per cent U_3O_8. The effect of the potassium was negligible, except in the region around 1·46 MeV represented by L_3. A solution was obtained from the intersection of the four remaining lines: 0·046 g U_3O_8 and 0·045 g ThO_2/100 g sample. The dis-

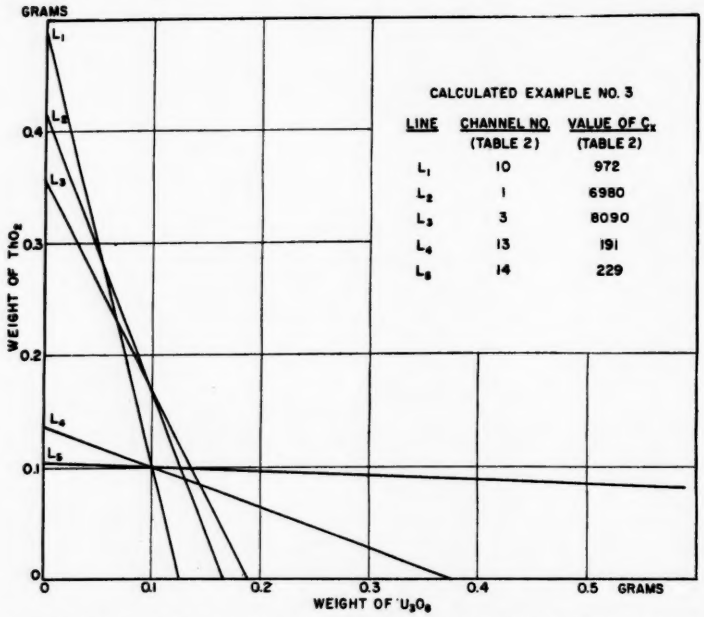

FIG. 5. Theoretical example for a mixture of U_3O_8, ThO_2 and purified U_3O_8 (equal weights of each).

low-energy channels, do not meet the common point of intersection of L_1, L_4 and L_5 which was obtained from the higher energy channels.

In Figs. 6 and 7 the effect of potassium-40 is illustrated. By consulting these figures and Table 2, an approximate lower limit may be set to the weight of K_2O which can be detected in the presence of other activity. Thus, in example 5 (Fig. 7) the effect on L_1 of 30 g of K_2O, when only U_3O_8 (0·1 g) and ThO_2 (0·1 g) were considered in the solution, can be seen.

Fig. 8 shows an actual solution of a crepancy in L_3 was attributed to potassium. Calculation gave the K_2O content as 9·8 g in a 100 g sample.

When more than two nuclide groups are present in detectable quantities in a sample, a solution should be obtained by working down the gamma-ray spectrum from the highest energy region, considering two groups at a time.

Solutions for several actual ore samples are summarized in Table 3; they are within the range of agreement of other methods of analysis. The graphical solutions for two typical samples are shown in Figs. 9 and 10.

CONCLUSIONS

The time required for the counting and calculation of a prepared sample is generally about 20 min; however, because the calculations remain somewhat complex, the

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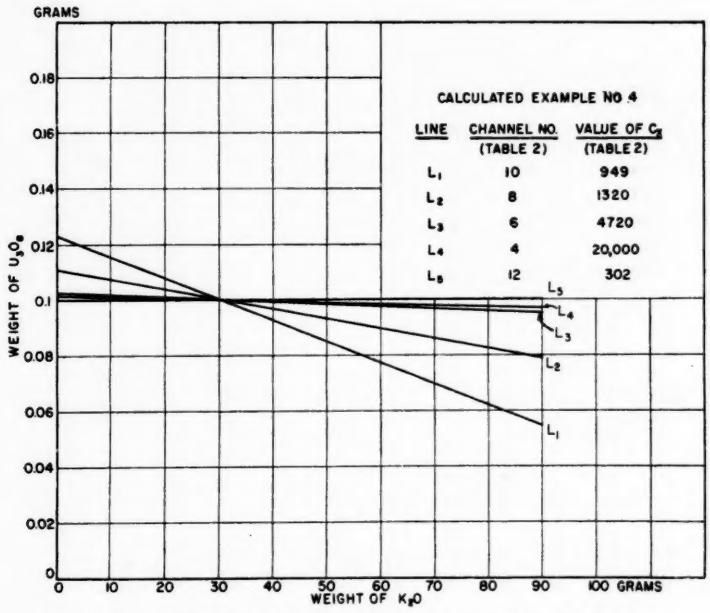


FIG. 6. Theoretical example for a mixture of U_3O_8 and K_2O.

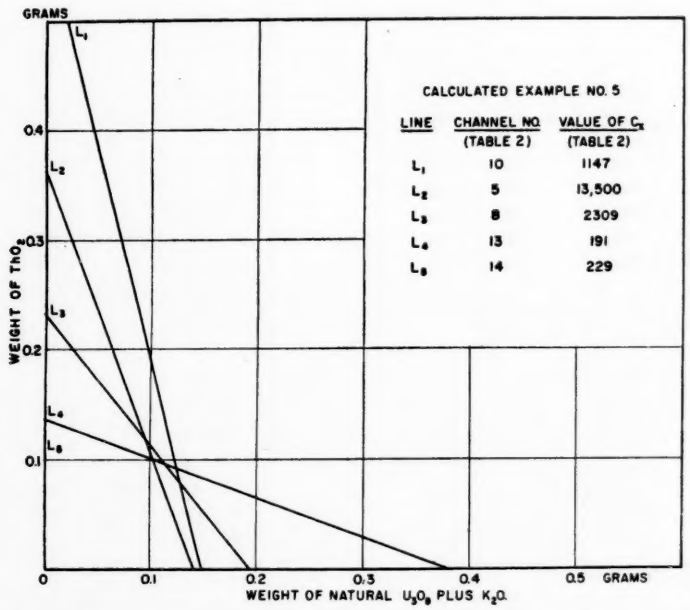
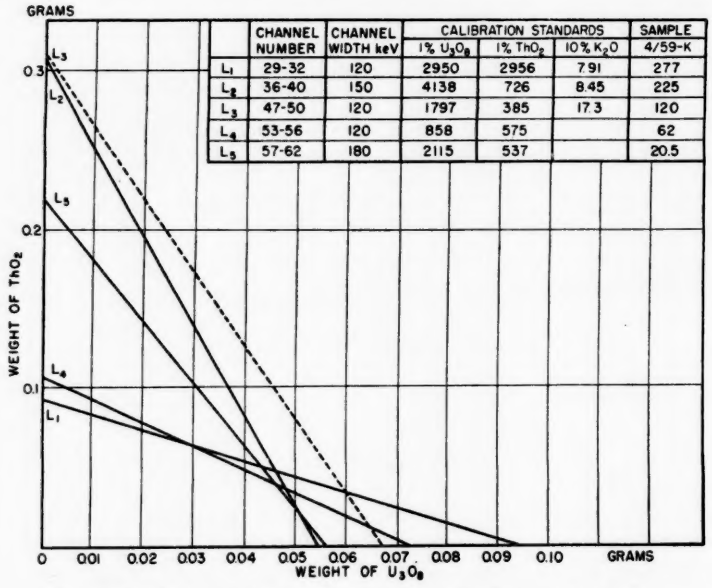


FIG. 7. Theoretical example for a mixture of ThO_2, natural U_3O_8, and K_2O.



	CHANNEL NUMBER	CHANNEL WIDTH keV	CALIBRATION STANDARDS 1% U_3O_8	1% ThO_2	10% K_2O	SAMPLE 4/59-K
L_1	29-32	120	2950	2956	7.91	277
L_2	36-40	150	4138	726	8.45	225
L_3	47-50	120	1797	385	17.3	120
L_4	53-56	120	858	575		62
L_5	57-62	180	2115	537		20.5

FIG. 8. Synthetic sample containing uranium, thorium, and potassium.

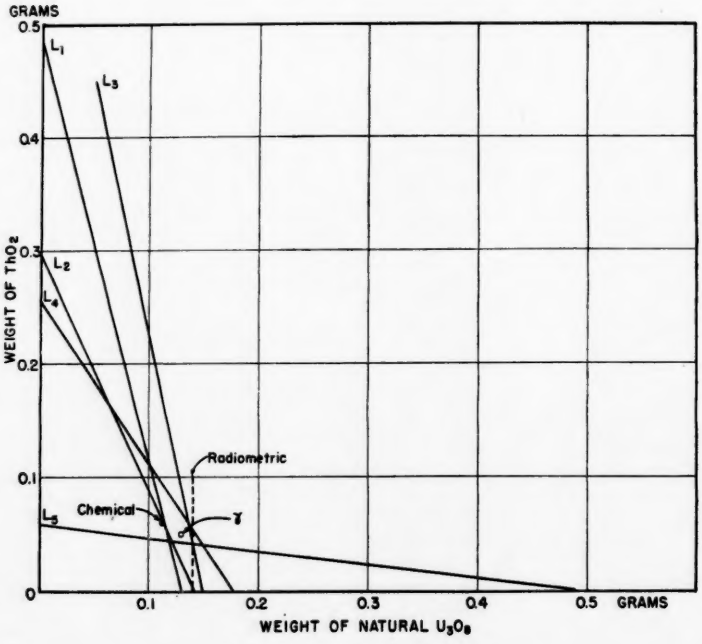


FIG. 9. Ore sample No. 269.

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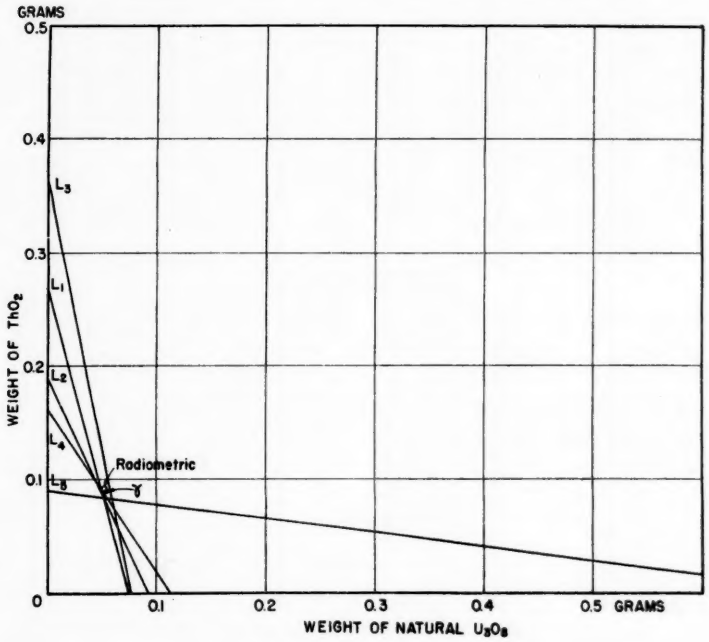

FIG. 10. Ore sample No. 362.

TABLE 3. Analysis of typical ore samples (percentage of weight)

Sample number	Chemical		Radiometric (β–γ)		Graphical (γ spectrometer)	
	U_3O_8	ThO_2	U_3O_8	ThO_2	U_3O_8	ThO_2
266	0·20	0·13	0·17	0·17	0·19	0·15
267	0·25	0·07	0·20	0·17	0·24	0·07
269*	0·11	0·06	0·14	—	0·13	0·05
362†			0·051	0·085	0·05	0·08
365			0·15	—	0·13	0·06
393			0·077	0·054	0·07	0·06
397			0·034	0·04	0·03	0·05

* Graphical solution shown in Fig. 9.
† Graphical solution shown in Fig. 10.

method would not be preferable to the usual radiometric methods except in a few instances: (a) when more than two radioactive components are present in a sample, (b) when the abundance of two components differs widely, for example, a thorium to uranium ratio greater than 10:1, (c) when the abundance of the components is low, and (d) as a non-destructive method of analysis (crushing of sample not required).

Additional time is required periodically to check the calibration, but this can be minimized by reducing sensitivity variations. Once adequate regulation of critical voltages has been achieved, the most serious factor affecting sensitivity is temperature change around the photomultiplier tube. The latter should be controlled to within 1°C. The walls of the lead castle shielding the sample should be lined with a light metal to reduce the lead X-ray peak at 73 keV.

To enable very small samples to be

analyzed by this method, and to improve the sensitivity through better sample geometry, a well-type detector could be employed as was done by HURLEY[6]. With a small sample, the effect of self-absorption would be reduced considerably below 100 keV. The well detector would not have as good a resolution, however, as has the cylindrical crystal used here.

Acknowledgements—The author wishes to express his thanks to Dr. G. G. EICHHOLZ for helpful discussions, to C. MCMAHON for the careful preparation of numerous samples, and to J. V. KRZYZEWSKI and J. M. LEFEBVRE for their assistance in operating and maintaining the equipment.

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APPENDIX

Sample calculation

Solution of example No. 1 (the graph is shown in Fig. 3).

In channel 10 (Table 2) *Cx* equals 970 counts for 10 min. Table 2 indicates that 0·1 g of natural ThO_2 yields 198 counts in 10 min and that 0·1 g of natural U_3O_8 yields 772 counts in 10 min.

Cx could have resulted from

$$\frac{970}{198} \times 0{\cdot}1 = 0{\cdot}49 \text{ g } ThO_2$$

or from

$$\frac{970}{772} \times 0{\cdot}1 = 0{\cdot}126 \text{ g } U_3O_8.$$

L_1 in Fig. 3 is obtained by plotting the latter two weights on the appropriate axes and then joining the points with a straight line. Similarly L_2, L_3, . . . are plotted from values obtained in channels 5, 4, ...

The lines intersect within a small area (a point in this idealized case) indicating the required weights of ThO_2 and U_3O_8 which contribute to the total count observed.

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Data for Industrial Irradiator Design from an Experiment to Reduced Scale

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Design data for industrial irradiation units may be obtained from measurements with a model to reduced scale. Validity and applicability of the method are discussed, and relations given between absorbed dose rate distributions within the model and full scale unit.

The results of a reduced scale experiment are applied to a determination of irradiator efficiency and prediction of throughput in a full scale unit containing a source of 150,000 curies Co^{60}. Dose rate distributions are examined within packages of various size.

DONNÉES POUR LE DESSIN D'UN IRRADIATEUR INDUSTRIEL OBTENUES D'UNE EXPÉRIENCE À ÉCHELLE RÉDUITE

On peut obtenir les données pour dessiner des unités destinés à l'irradiation industrielle au moyen d'un modèle à échelle réduite. On discute la validité et l'applicabilité de la méthode et on donne le rapport entre les distributions de taux de dose absorbée dans le modèle et dans l'unité de pleine grandeur.

Les résultats d'une expérience à échelle réduite s'appliquent à une détermination de l'efficacité de l'irradiateur et à la prédiction de la capacité de roulement dans un unité de pleine grandeur contenant une source de 150.000 c de Co^{60}. On observe les distributions de taux de dose dans des paquets de différentes grandeurs.

ДАННЫЕ ПО КОНСТРУКЦИИ ПРОМЫШЛЕННЫХ УСТАНОВОК ДЛЯ ОБЛУЧЕНИЯ, ПОЛУЧЕННЫЕ ИЗ ИЗМЕРЕНИЙ НА МОДЕЛЯХ РАЗЛИЧНЫХ МАСШТАБОВ

Данные по конструкции промышленных установок для облучения были получены из измерений на моделях различных масштабов. Обсуждаются ценность и применимость метода и приводятся зависмости между распределением активности в опытных условиях на различных моделях.

Результаты исследований на малых моделях использованы для определения эффективности и пропускной способности промышленной установки с источником Co^{60} в 150.000 кюри. Исследовано распределение активности в образцах разных размеров.

AUS EINEM EXPERIMENT IN VERKLEINERTEM MASSTABE GEWONNENE DATEN FÜR EINE INDUSTRIELLE BESTRAHLUNGSANLAGE

Planungsdaten für industrielle Bestrahlungsanlagen können aus Modellmessungen in verkleinertem Masstabe erhalten werden. Die Gültigkeit und Anwendbarkeit der Methode wird diskutiert, und es werden Beziehungen angegeben über die Verteilung der absorbierten Strahlungsdosen im Modell und der ausgeführten Anlage.

Die Ergebnisse eines Experimentes in verkleinertem Masstabe werden für die Bestimmung der Wirksamkeit der Strahlungsquelle angewendet und daraus Voraussagen für die Durchführung im vollen Masstabe bei Verwendung einer Quelle von 150,000 c Co^{60} gefolgert. Die Verteilung der Bestrahlungsdosis in Proben verschiedener Grösse wird geprüft.

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INTRODUCTION

An industrial radiation processing unit must operate with high efficiency since the cost and scarcity of radioactive material greatly affect the economic desirability of the process. Efficient use of radiation is achieved by proper choice of irradiator geometry. Ideally the source should be completely surrounded by process material so that the solid angle of escaping radiation is reduced to zero; the thickness of material should be large, in order to absorb as much as possible of the incident radiation. In practice it may be necessary to sacrifice some solid angle utilization in order to simplify process material handling problems. Furthermore, the amount of energy absorbed per gramme at any point, i.e. absorbed dose, falls off with distance from the source, and thickness is restricted so that the absorbed dose, at any point, lies within specified limits.

The design of an irradiator to fulfil a given dose rate specification with known efficiency requires a knowledge of dose rate distributions for a variety of source and sample geometries. Data may be obtained by laborious and refined calculations or by determining dose rates experimentally with full scale low intensity models of proposed geometries.

A further method is described here, which provides experimental information when a full-scale model is impracticable. Dose rates are determined within a model to reduced scale. All linear dimensions in the model are a fixed fraction of the corresponding dimensions of the unit, so that the relative distribution of incident radiation is unchanged. The distribution of radiation within the process material may be correctly reproduced in the model, provided density is suitably adjusted and the effective atomic number is unchanged.

The model source does not, however, reproduce the self absorption characteristics of the full scale unit, and this factor needs separate consideration. The following discussion is in terms of effective source strength, as deduced from a measurement of emitted radiation; the actual total source strength may be estimated by proper allowance for self absorption.

Measurements have been carried out using this method to determine the distribution of absorbed dose within a rectangular block of absorbing medium, simulating the irradiation geometry of a proposed package irradiation unit. The results are applied to a determination of irradiator efficiency and to the variation of absorbed dose within packages of various size.

VALIDITY OF REDUCED SCALE EXPERIMENT

Consider a point source emitting S photons/sec, irradiating a small element of volume dv as in Fig. 1(a). The photon flux incident on dv is $S/4\pi r^2$, where r is the distance from source to dv. The number of photons scattered per unit solid angle in the direction θ is

$$\mathrm{N}(\theta) = (\mathrm{S}/4\pi r^2)\rho\, dv\, \frac{d\sigma(\theta)}{d\Omega}$$

where $d\sigma(\theta)/d\Omega$ is the appropriate scattering cross-section in cm^2/g[1] and ρ is the density of scattering material. The flux of radiation at P, distance b from dv and a from the source, is $N(\theta)/b^2$ due to scatter from dv and $S/4\pi a^2$ direct from the source.

Figure 1(b) shows a scale model of 1(a), the scale factor is denoted by ε. The model element volume is $\varepsilon^3\, dv$ and the incident flux is $S/4\pi\varepsilon^2 r^2$. The total number of photons in the full scale system incident on $\varepsilon^3\, dv$ is, however, equal to the number incident on dv; for model and unit to have the same relative distribution of radiation, the model element must scatter the same number of photons as the full scale element dv, i.e.

$$(S/4\pi\varepsilon^2 r^2)\rho'\varepsilon^3\, dv\, \frac{d\sigma(\theta)}{d\Omega} = (S/4\pi r^2)\rho\, dv\, \frac{d\sigma(\theta)}{d\Omega} \qquad (1)$$

where ρ' is the density of model scattering element. Relation (1) requires that $\rho' = \rho/\varepsilon$ so that the model material must

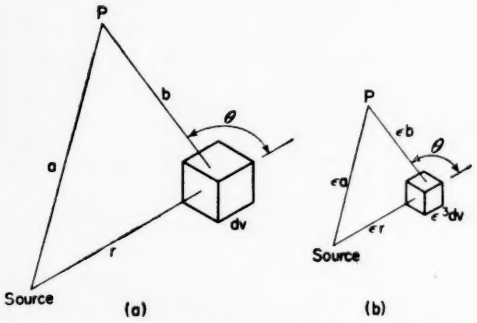

FIG. 1. The relative orientation of source, scattering element dv and point P shown in (a), are reproduced with a scale factor ($\varepsilon < 1$) in the model system (b).

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have a higher density than the unit process material; effective atomic number and photon energy remain unchanged. The flux of radiation at the point in the model corresponding to P is now $N(\theta)/\varepsilon^2 b^2$ due to scatter and $S/4\pi\varepsilon^2 a^2$ direct from source, so that the ratio of direct to scattered flux is preserved.

Dose rate is proportional to flux, the constant of proportionality depending on photon energy, hence dose rates within the model are $1/\varepsilon^2$, larger than the corresponding values within the unit. If model and unit source strengths are different and equal to S_m and S_u photons/sec respectively, then the ratio of dose rate at a point in the model to that at the corresponding point in the unit is $D_m/D_u = S_m/\varepsilon^2 S_u$. This relation is to be expected since, if $S_m \equiv S_u$, equal numbers of photons are incident on corresponding volume elements and the amount of energy deposited is the same. The energy absorbed in dv is $D_u \rho\, dv$, and in $\varepsilon^3\, dv$ is $D_m(\rho/\varepsilon)\varepsilon^3\, dv$, hence $D_m/D_u = 1/\varepsilon^2$.

Clearly the above considerations may be extended to an array of scattering elements and so to large volumes. Since any extended source may be replaced by a distribution of point sources, the model is valid for any geometry. A similar discussion has been given by FAILLA[2] in a paper on the effect of local density fluctuations on the response of ion chambers. The relations between unit and model are summarized in Table 1.

TABLE 1. Relations between unit and model

	Unit	Model
Scale factor	1	ε
Dimension	x	εx
Sample density	ρ	ρ/ε
Effective source strength	S_u	S_m
Dose rate	D_u	$D_u S_m/\varepsilon^2 S_u$

To apply the method, material of appropriate density and atomic number is required for the model. Choice of materials is eased by the fact that photon energies of interest lie close to 1 MeV, so that energy dissipation is largely by Compton scattering which depends only on the number of electrons per gramme. In addition, materials of interest commonly have low atomic numbers and bulk densities of less than unity.

EXPERIMENTAL DETAILS

Irradiations were carried out in the cobalt-60 unit 10K1 at Wantage Radiation Laboratory.[3] This unit has four line sources, each 32 in. long, which may be exposed in an adjustable array inside a concrete shield. The dimensions of the irradiation geometry of a proposed industrial unit are given in Table 2, together with the dimensions of the reduced scale experimental assembly. The scale factor 2·55 was determined by the 10K1 source size. The four line sources were arranged in a vertical plane with 3 in. between centres to provide a fair approximation to the irradiator source shape.

Materials under consideration for treatment have bulk densities of the order of 0·3–0·5, and hence material of density 0·75–1·30 was required for the experimental absorbing medium. Perspex sheet was selected as a suitable material, combining convenient physical form with low atomic number and a density of 1·19.

TABLE 2. Dimensions of unit and model

Scale factor = 2·55	Industrial unit (in.)	Scale model (in.)	Dimensions used (in.)
Source length	82	32·3	32·0
Source width	24·5	9·6	9·6
Package array length	112	43·9	48
Package array width	64	25·1	24
Package array thickness	9	3·53	3·75
Distance between source and package array	6·75	2·65	2·65

Five sheets of 0·75 in. thick perspex sheet were clamped together to form a block of dimensions 48 × 24 × 3·75 in. One sheet was drilled to accommodate ferrous sulphate dosimeter ampoules for the absorbed dose measurements. The five sheets were held in position by the irradiation jig shown in Fig. 2, and the assembly was irradiated five times with the dosimetry sheet occupying each of the five sheet positions in turn.

Dosimeter positions are conveniently specified with respect to axes OX, OY and OZ taken parallel to the sides of length 48, 24 and 3·75 in. respectively, with origin at the face centre nearest the source. Measurements were made in one quarter of the block at positions denoted by the intersections of $X = 0$, 10, 13, 17, 22, $Y = 0$, 3·00, 5·50, 8·50, 11·50 and $Z = 0·375$, 1·125, 1·875, 2·625, 3·375. The absorbed dose distributions over the remaining quarters were inferred from symmetry. The dosimeter readings are plotted in Figs. 3–7 to give the distribution of absorbed dose throughout the block.

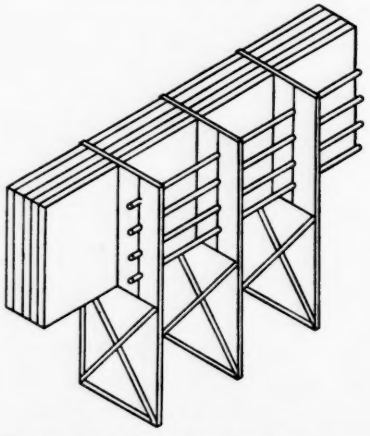

FIG. 2. Irradiation assembly, showing the perspex sheets held in position parallel to the four Co^{60} line sources.

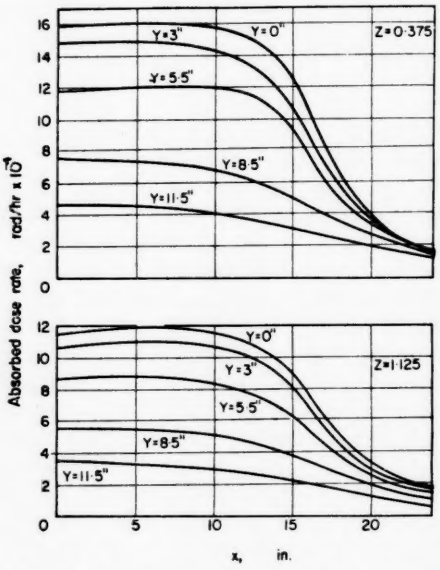

FIG. 3. Absorbed dose rate within first perspex sheet.

FIG. 4. Absorbed dose rate within second perspex sheet.

APPLICATION OF RESULTS

Energy absorption efficiency. The curves of Figs. 3–7 were integrated numerically to find the mean dose rate over planes parallel to the source. The resulting values are

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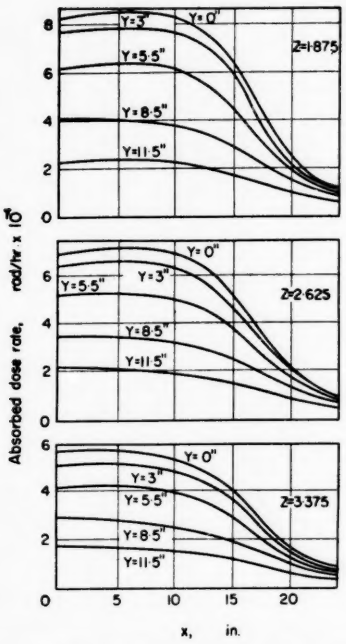

FIG. 5. Absorbed dose rate within third perspex sheet.

FIG. 6. Absorbed dose rate within fourth perspex sheet.

FIG. 7. Absorbed dose rate within fifth perspex sheet.

plotted in Fig. 8 against distance through the slab.

The total γ-ray energy emitted by the source was estimated by comparing calculated dose rates in air at various distances from the source, with measurements by ferrous sulphate dosimeter. The effective curie strength found in this way is 4640, and the total radiated energy is 68·7 watts or $6{\cdot}87 \times 10^6$ g rad/sec.

The curve of Fig. 8 was next integrated for a number of block thicknesses and multiplied by the absorbing mass, to give the energy absorbed in g rad/sec. The values were then multiplied by 2, since the actual irradiator would utilize both sides of the source, and were divided by the total radiated energy output per second. The resulting curve, plotted in Fig. 9, gives the fraction of energy absorbed in slabs of varying thickness

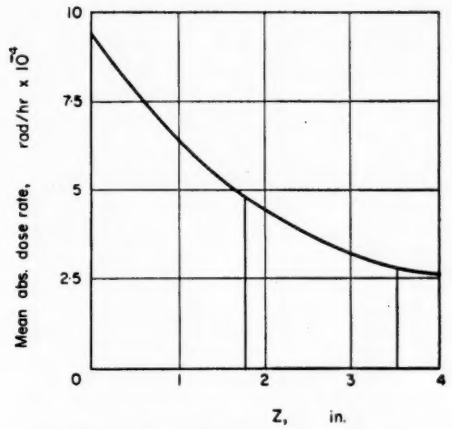

FIG. 8. Mean absorbed dose rate vs. Z.

placed symmetrically on either side of the source. The energy absorption efficiency may now be read off from Fig. 9 for given thickness of absorbing layer. A convenient thickness under consideration for the irradiator is 9 in., corresponding to 3·53 in. of perspex and hence to an absorption of 33 per cent of the total energy.

The distribution of absorbed dose. In a practical arrangement the absorbing block consists of an array of packages passing through the irradiator by automatic conveyor. The array of packages consists of two rectangular banks placed symmetrically on either side of the source (the perspex block

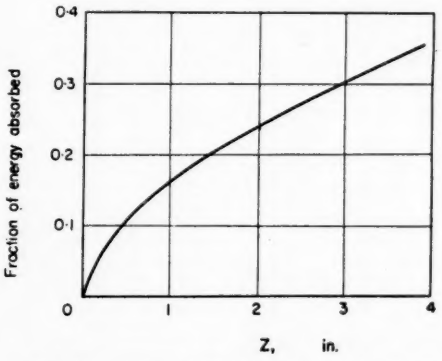

FIG. 9. Energy absorbed in two equal rectangular slabs of perspex as a fraction of the total energy radiated by a rectangular plane source placed symmetrically between them.

simulates one bank). Packages enter the top of one bank, traverse the top row in a series of movements and rests to the end of the row, then descend to a lower row and repeat until the last position in the bank is occupied.

Each package then crosses to the opposite bank and repeats the process, moving upwards this time, finally emerging from the end of the topmost row. It should be noted that the time spent in moving from one position to the next is small compared with the "rest" period. Because the packages occupy each position in sequence on both sides of the source without changing their orientation, the variation of dose within each package is to a large extent balanced out, but not completely so.

The distribution of absorbed dose is important since packages are generally to be processed to a specified minimum dose, not mean dose, and overdosing represents wasted energy. In addition, overdosing may well be undesirable from other considerations. The calculation of the minimum dose rate, however, is laborious and depends on package size, whereas the mean is constant for a given array and provides a measure of "goodness" of package size.

Effect of package size. The distribution of absorbed dose within a package may be estimated by adding up dose contributions to different positions within the package whilst it traverses the path of the conveyor.

The relative distribution of dose within a package of full-scale size 12·8 × 14 × 9 in., obtained by occupying all 5 × 8 positions within the two blocks, is given in Table 3. The key to Table 3 is given in Fig. 10.

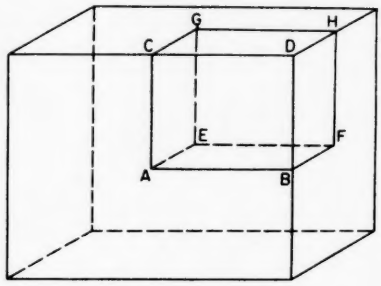

FIG. 10. Key to Table 3.

TABLE 3. Distribution of dose rate within a package of size 12·8 × 14 × 9 in.

Position within package	Dose rate (% about mean)
A	+21·6
B	+21·2
C	+16·4
D	+15·3
E	−11·8
F	−12·4
G	−13·5
H	−14·1

The maximum and minimum dose rates for several package sizes are given as a percentage of the mean in Table 4. Inspection of this table shows that there is little advantage in decreasing package size from 32 × 28 × 9 to 12·8 × 28 × 9 or in further decreasing it to 12·8 × 14 × 9 in., although the smallest size may perhaps be preferred for handling or other reasons.

This illustrates a useful principle: evidently with very small packages, uniformity

TABLE 4. Maximum and minimum dose rates within packages of different sizes

Package size, (in.)	Number in each vertical column and horizontal row		Maximum dose rate above mean (%)	Minimum dose rate below mean (%)
	C.	R.		
64 × 112 × 9	1	1	129·0	87·5
32 × 56 × 9	2	2	41·0	38·0
32 × 28 × 9	2	4	22·7	19·1
12·8 × 28 × 9	5	4	22·3	14·9
12·8 × 14 × 9	5	8	21·6	14·1

TABLE 5. Mean dose rate and efficiency of irradiator

	Model	Industrial unit	
Density of absorbing material	1·19	0·47	g/cm³
Effective source strength	4640	150,000	curies
Mean absorbed dose rate	$5{\cdot}24 \times 10^4$	$1{\cdot}93 \times 10^5$	rad/hr
Minimum dose rate over package 12·8 × 14 × 9	$4{\cdot}50 \times 10^4$	$1{\cdot}65 \times 10^5$	rad/hr
Efficiency*	28·3%	28·3%	—
Throughout*	0·17	5·3	Mrad ton/day

* Not corrected for absorption in conveyor system or for spaces between packages.

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of dose improves as size decreases; however, when the array consists of relatively few large packages, certain sizes may exist which fit the dose distribution curves with more uniform dosing than other possibly smaller sizes. Fig. 11 illustrates this point with an idealized one-dimensional distribution curve where packages *A* achieve better averaging than the smaller packages *B*.

It should be noted that the energy absorbed by the package array will be reduced by self-absorption in the source, by absorption within the conveyor system and by escape through the gaps between packages.

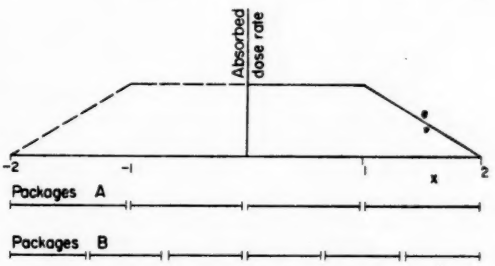

FIG. 11. Idealized one dimensional absorbed dose curve. Packages rest for equal times at consecutive positions in passing along curve. More uniform averaging is achieved by the packages *A* than by the smaller packages *B*.

SUMMARY

The characteristics of the experimental irradiation geometry and the corresponding values for a full-scale unit are given in Table 5. The measurements indicate that a throughput of the order of 5 Mrad ton/day may be obtained with a unit employing 150,000 curies of Co^{60}.

Acknowledgement—The authors wish to thank Mr. S. W. PIGOTT for assistance in preparing the drawings.

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Investigations on Chemical Properties of Francium by Means of Fr^{212}

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The present paper concerns a generalization of work on the chemistry of francium carried out by means of Fr^{212}. Methods for recovery and isolation of francium isotopes are considered. Co-precipitation of Fr^{212} with various precipitates is studied. Most extensive are studies on co-precipitation of francium, caesium and rubidium with di- and tri-heteropoly acids. Volatilities of tracer quantities of francium and caesium chlorides are studied as a function of temperature and time of heating. Detailed investigation is made on the sequence of adsorption of francium, caesium and rubidium cations on KU-1 and KU-2 cation exchangers from electrolytic solutions of different concentrations. A new method of rapid and effective isolation of francium from caesium and rubidium is worked out. The possibility of using Fr^{223} for the determination of actinium in uranium ores is shown.

RECHERCHES SUR LES PROPRIÉTÉS CHIMIQUES DU FRANCIUM AU MOYEN DU Fr^{212}

Cette communication fait un récit général du travail sur la chimie du francium achevé au moyen du Fr^{212}. On considère des méthodes de récupérer et d'isoler les isotopes de francium; on étudie la co-précipitation du francium, du caesium et du rubidium avec des acides di- et tri-hétéro-poly forme plus particulièrement parmi les études de la co-précipitation du Fr^{212} avec des précipités divers. On examine la volatilité des chlorures de francium et de caesium en quantités indicatrices en rapport à la température et à la durée du chauffage. On fait une recherche détaillée sur la suite de adsorption des cations de francium, de caesium et de rubidium sur les échangeurs cationiques KU-1 et KU-2 hors des solutions électrolytiques de différentes teneurs. On donne le développement d'une nouvelle méthode pour séparer rapidement et effectivement le francium du caesium et du rubidium. On démontre la possibilité d'employer le Fr^{223} pour le dosage de l'actinium dans les minérais d'uranium.

ИЗУЧЕНИЕ ХИМИЧЕСКИХ СВОЙСТВ ФРАНЦИЯ С ПОМОЩЬЮ Fr^{212}

Настоящая статья посвящена обобщению работ по химии франция, выполненных авторами с помощью Fr^{212}. Рассмотрены методы получения и выделения изотопов франция. Изучено соосаждение Fr^{212} с различными осадками. Наиболее подробно исследовано соосаждение франция, цезия и рубидия с ди- и тригетерополикислотами. Определены летучести индикаторных количеств хлоридов франция и цезия в зависимости от температуры и времени нагревания. Проведено детальное исследование сорбируемости катионов франция, цезия и рубидия на смолах КУ-1 и КУ-2 из различных концентрированных растворов электролитов. Разработан новый метод быстрого и эффективного отделения франция от цезия и рубидия. Показана возможность применения Fr^{223} для определения актиния в урановых рудах.

ERFORSCHUNG DER CHEMISCHEN EIGENSCHAFTEN DES FRANCIUM MIT HILFE VON Fr^{212}

Der vorliegende Artikel bringt eine Zusammenfassung der mit Fr^{212} über die Chemie des Francium durchgeführten Arbeit. Gewinnungs—und Trennungsmethoden von Franciumisotopen werden betrachtet. Die Mitfällung des Fr^{212} an verschiedenen Niederschlägen wird untersucht. Am ausführlichsten sind die Untersuchungen über die Mitfällung des Francium, Cäsium und Rubidium an Zwei—und Dreiheteropolysäuren. Über die Flüchtigkeit von Spurenmengen des Franciumchlorid und Cäsiumchlorid als Funktion der Temperatur und der Dauer der Erhitzung wird gearbeitet. Genaue Untersuchungen über due Reihenfolge der Adsorption von Francium-, Cäsium- und Rubidiumkationen an KU-1 und KU-2 Kationenaustauschern aus Elektrolytlösungen verschiedener Konzentration werden angestellt. Eine neue Methode für eine rasche und wirksame Trennung des Francium von Cäsium und Rubidium wird ausgearbeitet. Die Möglichkeit der Verwendung von Fr^{223} für die Bestimmung des Actinium in Uranerzen wird gezeigt.

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THE existence of an element No. 87 was predicted in 1870 by MENDELEEV[1] who wrote at the time that this element must be placed in the first group of the tenth series of the periodic system of elements, have an atomic weight of 210–230, form an oxide of R_2O composition and be an analogue of caesium.

An element of $Z = 87$ was first reported in 1925 by DOBROSERDOV[2] who gave it the name of "russium". Soon after, however, his and many other works[3–5] carried out in order to establish the natural abundance of stable isotopes of the element No. 87 were found to be erroneous. As far back as 1914 detailed investigations on radioactive decay of uranium and thorium series conducted by MEYER *et al.*[6] lead these authors to a suggestion as to the formation of a radioactive francium isotope by α-decay of actinium. However, PEREY[7] succeeded in recovering and investigating the chemical nature of this isotope only 25 years after. Beginning with 1939 and up to the present time she studied certain chemical and other francium properties by means of the Fr^{223} isotope.[7–10] A large amount of interesting information was obtained in these studies.

In 1956 the authors began systematic investigations of francium properties that were yet unknown, and attempted to find means for the recovery of its isotopes. Special attention was given to the working out of methods for isolating short-lived active francium from caesium and rubidium. The present paper will be concerned with experimental works carried out in this respect.

CLASSIFICATION OF FRANCIUM ISOTOPES AND METHODS FOR THEIR RECOVERY

Evidence on eight radioactive isotopes is available at present[11] (Table 1). The longest lived ($T \simeq 20$ min) are Fr^{212} and Fr^{223}. Since the study of francium properties by means of these isotopes is connected with many difficulties, a question arose as to the possibility of predicting longer-lived isotopes on the basis of isotope classification.

Fig. 1 shows α-decay energies of known francium, astatine and polonium isotopes as a function of the number of neutrons. Of great importance in predicting values for α-decay energies would be the fact that maximum α-decay energy and consequently shortest half-life periods are observed for isotopes of $N = 128$. Fr^{215} is such an isotope of francium. Extrapolation of the line connecting heavy francium isotopes of $A = 221$–217 (Fig. 1) to its intersection with the ordinate corresponding to $N = 128$ makes possible the estimation of α-decay energies for Fr^{215} and Fr^{216}. On the analysis of the curves for light isotopes of emanation, astatine and polonium shows that isotopes containing 125 neutrons have the minimum α-decay energy. Fr^{212} belongs to these isotopes. By analogy with the shape of curves for the above-mentioned isotopes in

TABLE 1. Data on properties and formation cross-sections of francium isotopes

Mass number	Type of decay	Half-life period	α-Particle energies (MeV)	Predicted α-decay energies (MeV)	Formation cross-section (σ) (mb)
210				6·7	0·04
211				6·7	0·09
212	α 44%, EC56%	19·3 min	6·409 (37%) 6·387 (39%) 6·339 (24%)		0·2*
213				7	0·3
214					0·5
215				9·3	0·9
216				8·7	1·5
217	α	Very short	8·3		2·2
218	α	5×10^3 sec	7·85		4·0
219	α	0·02 sec	7·30		5·6
220	α	27·5 sec	6·69		6·8
221	α	4·8 min	6·30 (75%) 6·05 (25%)		
222	$\beta^- > 99\%$, α(0·01–0·1%)	14·8 min			1·5
223	$\beta^- > 99\%$, $\alpha(4 \times 10^{-3}\%)$	21 min	5·34 $\beta^- - 1{\cdot}2$		0·6
224					0·2
225					0·06

* Experimental value.

Fig. 1, it is possible to draw a similar region for francium isotopes having the same number of neutrons. Alpha-decay energies of Fr^{213}, Fr^{211} and Fr^{210} can be found from this plot. Values obtained by one of the

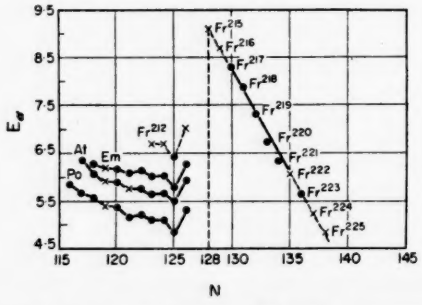

FIG. 1. Energy of α-decay of francium, emanation, astatine and polonium isotopes as a function of the number of neutrons.

authors[12] on the α-decay energy of the above-mentioned isotopes are given in Table 1.

Comparison of experimental and predicted evidence on α-decay energies of francium isotopes displaying only α-activity shows that the maximum α-decay energy is observed for Fr^{212} ($T = 19{\cdot}3$ min) and Fr^{221} ($T = 4{\cdot}8$ min). E_α values for all other isotopes are considerably higher and their half-lives are consequently shorter. Hence there is no reason to expect a more long-lived isotope than Fr^{212} among α-active francium isotopes.

Beta-decay is predominant with francium isotopes of $A \geqslant 222$. Half-lives of β^--active isotopes are known generally to decrease with increase of the excess of neutrons in the nuclei. Thus an isotope of a longer half-life than that of Fr^{223} could scarcely be found among the heaviest francium isotopes.

Detailed investigations on fission products of natural radioelements carried out by a number of authors have shown that Fr^{223} is an intermediate link in the actinium–uranium series, and Fr^{221} in the neptunium series. These isotopes may be found in uranium ores and minerals. All other francium isotopes can be obtained only artificially. Most effective methods for recovery of francium isotopes consist in bombardment of heavy uranium and thorium elements with high-energy particles, and of

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bismuth or lighter elements with multiply charged ions of high energy.

Fr^{223} can also be obtained in a nuclear reactor by reaction

$$Ra^{226}(n,\gamma)Ra^{227} \xrightarrow[41{\cdot}2\ \text{min}]{\beta^-} Ac^{227} \xrightarrow[1{\cdot}2\ \text{per cent}]{\alpha} Fr^{223}.$$

The cross-section (n,γ) of the reaction on Ra^{226} is large (~51 barn).[13] Consequently sufficient quantities of Ac^{227} can be accumulated on prolonged bombardment, thus ensuring a constant source of Fr^{223}.

The authors have determined the cross-section for Fr^{212} formation by reaction $U^{238}(p,6p21n)Fr^{212}$ in irradiation of uranium metal with 660 MeV protons.[14] It appeared to be 0·2 mb. By interpolating cross-sections found for isotopes of neighbouring elements of radium, astatine and others, it was possible to determine the approximate shape of the curve for formation cross-sections of a number of francium isotopes as a function of their mass numbers (Fig. 2). Estimated values of cross-sections for the formation of francium isotopes over a range of A from 210 to 225 are summarized in Table 1. As can be seen from the Table, on spallation of uranium by 660 MeV proton bombardment maximum yields are obtained of short-lived isotopes, Fr^{218}, Fr^{219}, Fr^{220} and Fr^{221}. The predicted value of the cross-section for Fr^{223} formation is 0·6 mb i.e. its quantity should be three times that of the formed Fr^{212}.

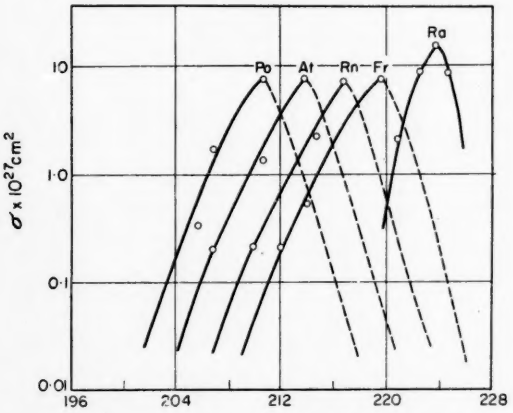

FIG. 2. Curves for distribution of yields in francium isotopes and neighbouring elements by their mass numbers during fission of uranium by bombardment with 660 MeV protons.

On bombarding 1 g of uranium metal with 660 MeV protons in the synchrocyclotron of the Nuclear Problems Laboratory of the Joint Nuclear Research Institute, (Dubno), 5×10^{-15} g of Fr^{212} of an activity $2{\cdot}5 \times 10^{-15}$ disintegrations/min were formed within 15 min. The activity of Fe^{223}, in accord to its predicted yield, should be $\sim 1 \times 10^8$ disintegrations/min. With a thorium target francium formation cross-sections will be slightly higher (up to double values). Thus the recovery of francium isotopes by means of thorium bombardment would be most feasible.

Cross-sections for francium isotope formation in reactions involving multiple charged ions are not yet investigated; however, from general theoretical considerations they would be considerably higher. Hence detailed studies of such reactions would be of great interest. The possibility of detecting new francium isotopes formed in reactions involving fast multiple charged ions is not excluded.

METHODS FOR ISOLATION OF FRANCIUM FROM IRRADIATED URANIUM AND THORIUM

The method for francium isolation must be very rapid and imply separation from the complex mixture of uranium and thorium fission and spallation products formed in high yields.

A target of uranium metal or of U_3O_8 weighing about 250 mg was bombarded for 15 min with 660 MeV protons in the internal synchrocyclotron beam at the Laboratory of Nuclear Problems of the Joint Nuclear Research Institute. The irradiated target was rapidly dissolved in a minimum amount of nitric acid in the presence of several droplets of H_2O_2. Caesium chloride (10–20 mg) was introduced as a non-isotopic carrier, the solution was diluted to 0·3 M with respect to HNO_3, 10 mg of bismuth nitrate were added and bismuth sulphide

was brought down with hydrogen sulphide. The sulphide precipitate was removed, the filtrate was boiled to eliminate H_2S, uranium hydroxide was precipitated with ammonia, 10 mg of ferric chloride was added to the filtrate, and ferric hydroxide was precipitated. The last procedure was carried out repeatedly. The filtrate was rapidly evaporated to dryness, the residue was dissolved in water, and caesium perchlorate was precipitated from the alcohol solution. The precipitate was again brought down and dissolved in water. The solution obtained, containing francium (Fr^{212} and Fr^{223}), caesium (Cs^{129}, Cs^{136} and Cs^{138}) and rubidium (Rb^{81}, Rb^{82} and Rb^{86}), was used in early experimental investigations on francium chemical properties.[15] The time of isolation was 35–40 min.

A francium isolation method based on the results of HYDE[16] was also used in the present work. With this method powdered thorium metal weighing about 200 mg was dissolved after bombardment in hydrochloric acid. Francium was precipitated with silicotungstic or phosphotungstic acid[15], the precipitate was dissolved in water and the solution was passed through a chromatographic column, 10–25 mm in dimensions and 4 mm in diameter, filled up with finely ground cation exchanger Dowex-50 or KU-2 (Russian mark). The heteropoly acid anion passed through the exchanger bed and Fr^+ and Cs^+ cations adsorbed on resin were expelled with concentrated hydrochloric acid. The eluent was evaporated and water was added to the residue. The resultant solution contained carrier-free active isotopes of francium, caesium and some rubidium. The time of isolation was 25–35 min.

As the isolated francium preparations contained β^--active isotopes of caesium and rubidium, they were measured only by the α-activity of Fr^{212}. For this reason the authors suggested a method for rapid preparation of α-active samples involving uniform distribution of the precipitate on the support surface.[15] The precipitate was mixed with an organic solvent, alcohol, ether or acetone, and transferred into a Plexiglas centrifugal test-tube with a base which could be unscrewed. A mica disk, 10 mm in diameter, was placed on the bottom and the suspension was centrifuged. The precipitate was then dried under an infra-red lamp. To prevent the precipitates from decrepitation the disks were covered with thin amylacetate films.

Alpha activity of Fr^{212} was measured by a scintillation counter having a crystal of ZnS (Ag) permitting measurements of the α-activity at a background of high β and γ activities. Relative errors in activity measurements amounted to 5–10 per cent depending upon the nature, uniformity and thickness of the samples.

The radiochemical purity of francium preparations was established by measuring the decay of isolated preparation activities. A curve for francium decay is given in Fig. 3.

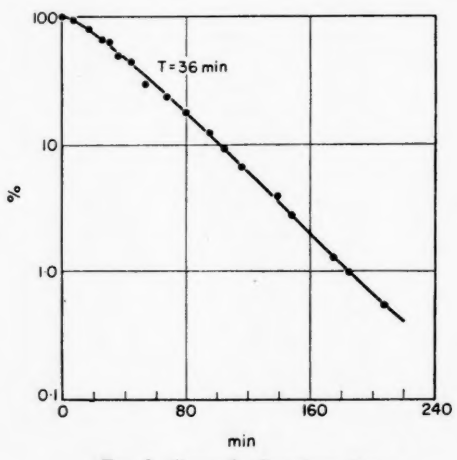

FIG. 3. Curve for francium decay.

It corresponds to $T = 35$ min. Calculations have shown that the value obtained is consistent with the scheme of Fr^{212} decay:

$$Fr^{212} \xrightarrow[19{\cdot}3\ \text{min}]{\text{EC(56 per cent)}} Em^{212} \xrightarrow[23\ \text{min}]{\alpha} .$$

It was shown in addition that the activity does not pass into the organic solvent on extraction with diethyl ether from 1·5 M nitric acid solution, with amyl alcohol from a 4·5 M hydrochloric acid and with a solution of tributylphosphate in CCl_4 from a 4 M nitric acid solution. This is evidence for the absence of other α-active elements that could have been extracted under these conditions.

Commercial preparations of Cs^{134} of a high specific activity were used in investigations. To obtain Rb^{86}, 10 mg of chemically pure rubidium sulphate was bombarded for about 40 hr in a nuclear reactor with a neutron flux of $8{\cdot}7 \times 10^{12}$ n/cm² sec. The radioactive purity of caesium and rubidium was determined from β-particle energies absorption in aluminium. Measurements were made by a counter MCT-17 (Russian mark). The statistical error in count was less than 5 per cent.

INVESTIGATION OF CERTAIN CHEMICAL PROPERTIES OF FRANCIUM

As there are no long-lived isotopes of francium it cannot be obtained in measurable amounts, in contrast to other artificial elements. For this reason all chemical properties of francium can be studied only with tracer quantities of short-lived isotopes. This hinders the studies considerably.

Of great interest in determining francium chemical properties are experiments on co-precipitation of francium with different precipitates. The results of these experiments are summarized in Table 2. They are in agreement with earlier data obtained by Perey. An assay of these data shows that francium does not co-precipitate with the majority of precipitates investigated, such as hydroxides and sulphides of various elements, barium carbonate, manganese dioxide, and silver chloride. Most complete co-precipitation of francium is observed with caesium chlorplatinate. Of interest is the fact that quantitative co-precipitation of francium with caesium and kalium perchlorates and with caesium dipicrylaminate was not observed. It will be noted that the amount of francium co-precipitated with perchlorates

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Table 2

Carr. No.	Carrier	Temperature	Precipitating agent	Experimental conditions	Amount of co-precipitated Fr^{212} (%)
1	$Ce(OH)_4$	100°C	NH_4OH	0·007 M $Ce(NO_3)_4$ in the presence of H_2O_2	0
2	$La(OH)_3$	Room	NH_4OH	0·007 M $La(NO_3)_3$, excess of precipitating agent	0
3	$Fe(OH)_3$	Room	NH_4OH	0·02 M $Fe(NO_3)_3$, excess of precipitating agent	0
4	$CsClO_4$	Room	$HClO_4$	0·01 M CsCl from an alcohol solution	60
5	$KClO_4$	Room	$HClO_4$	0·03 M KCl from an alcohol solution	60
6	$BaCO_3$	Room	Na_2CO_3	0·007 M $BaCl_2$	0
7	$CsBiCl_6$	Room	c.c.*		90
8	$CsPtCl_6$	Room	H_2PtCl_6	(a) 0·01 M CsCl, excess of H_2PtCl_6	100
				(b) 0·005 M H_2PtCl_6, excess of CsCl	100
9	PbS	Room	H_2S (gas)	0·005 M $Pb(NO_3)_2$, 0·3 M HNO_3	0
10	Bi_2S_3	Room	H_2S (gas)	0·005 M $Bi(NO_3)_3$, 0·3 M HNO_3	0
11	MnO_2	100°C	$KMnO_4$	0·02 M $MnSO_4$	0
12	MnO_2	Room	$KMnO_4$	0·02 M $MnSO_4$	0
13	Te	Room	$SnCl_2$	0·008 M H_2TeO_4, in HCl	0
14	Te	Room	H_2SNO_3	0·008 M H_2TeO_4, in NaOH	0
15	Caesium dipicrylaminate	Room	c.c.*	0·01 M CsCl, excess of ammonia dipicrylaminate	50
16	AgCl	Room	HCl	0·01 M $AgNO_3$, excess of 0·1 M HCl	0

* c.c. Denotes the co-precipitated carrier.

is independent of the microcomponent nature. Changes in the sequence of carrier and precipitating agent additions on precipitation of caesium chlorplatinate have no effect on the degree of francium co-precipitation. This points to possible isomorphous co-precipitation.

INVESTIGATIONS ON METHODS FOR FRANCIUM ISOLATION FROM OTHER ALKALI ELEMENTS

One of the up-to-now unsolved problems in francium chemistry was the problem of its isolation from caesium and rubidium. In view of the possible application of francium in diagnostics of malignant tumours[17] the necessity arises to separate it from β-active and long-lived rubidium and caesium isotopes obtained in uranium and thorium fission. This would also make possible the use of Fr^{223} formed in considerably higher yields than Fr^{212} in chemical investigations. Thus the given problem becomes very up to date. Most appropriate for its solution would be the method[18] for sublimation of halide compounds, co-precipitation with heteropoly acids and ion-exchange chromatographic separation.

(1) *Investigations on the volatility of francium and caesium chlorides*

No information has yet been reported on the volatility of francium chloride. Thus, investigation of tracer quantities of francium as a function of temperature and heating was of an unquestionable interest. In this connexion aliquots of a neutral francium chloride solution were deposited on flat platinum disks 15 mm in diameter, dried and heated at temperatures within 200°–1000°C from 4 to 20 min. Analogous experiments were carried out with 2×10^{-8} g of CsCl. Obtained results are shown as four plots in Fig. 4, where every plot corresponds to a definite heating time. The figure also shows volatility isotherms of francium chloride (the isotherm corresponding to 500° was obtained by interpolation). As can be seen from obtained results, differences observed in sublimation of tracer quantities of caesium and francium chlorides are insignificant. Consequently separation of francium and caesium chlorides by sublimation appears to be ineffective under experimental conditions.

2. *Studies of co-precipitation of francium and caesium with heteropoly acids*

Co-precipitation of kalium, rubidium and caesium with diheteropoly acids is known to have found application in the technique of their separation by analytical chemistry and radiochemistry means. Considerably lesser differences in radii of francium and caesium cations obviously lead to greater difficulties in their separation as compared with other alkali elements. However, the possibility is not excluded that just heteropoly acids forming difficultly soluble compounds of a high molecular weight might provide means for caesium and francium separation. For this reason the authors have studied co-precipitation of Fr^{212} and Cs^{134} with free di- and tri-heteropoly acids.

(a) *Co-precipitation of francium and caesium with diheteropoly acids.* Diheteropoly acids are known to form difficultly soluble precipitates in strong acid solutions. Co-precipitation of alkali metal cations with precipitates of free diheteropoly acids were not studied extensively, and consequently this problem is of self-importance whether or not differences will be found in the degree of francium and caesium co-precipitation.

The following technique was applied in experiments. Solutions of hydrochloric acid, 10 N, and a set volume of Fr^{212} and Cs^{134} solutions of an activity $(10–20) \times 10^3$ impulses/min, and in certain experiments 0·5 mg of caesium, ferrum and bismuth as chlorides were introduced into Plexiglas test-tubes with bases which could be unscrewed. A corresponding heteropoly acid solution was then added in such an amount as would ensure a precipitate weight not higher than 3–5 mg, and an overall solution volume not exceeding 1 ml. The precipitate was centrifuged, washed, the test-tube bottom was unscrewed and put under the light

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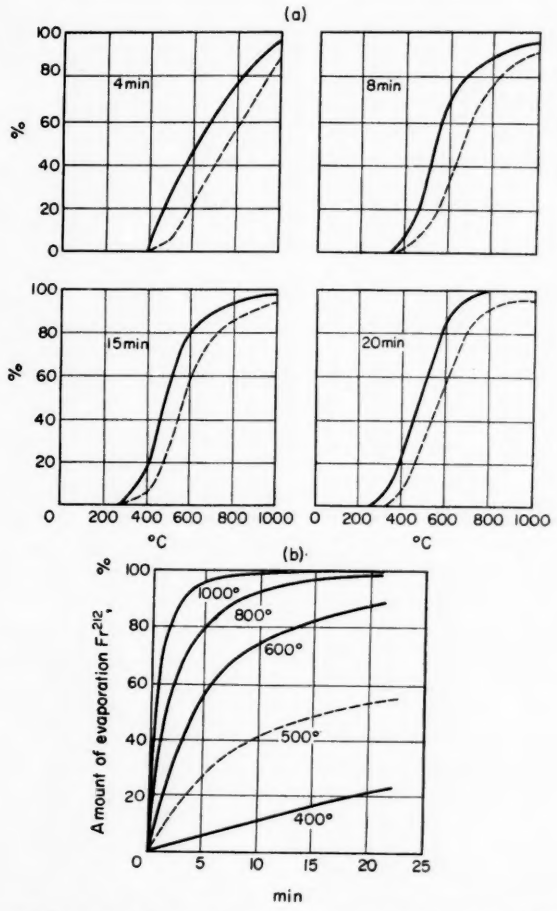

FIG. 4. Volatility of FrCl and CsCl, as a function of temperature (a), and the FrCl volatility isotherm (b).

of an infra-red lamp in order to dry the precipitate; its activity was then measured.

The results of a number of experiments on co-precipitation of tracer quantities of Fr^{212} and Cs^{134} with diheteropoly acids, such as silicotungstic (abbreviated definition HSiW), phosphotungstic (HPW), silicomolybdenum (HSiMo) and phosphomolybdenum (HPMo) from 10 N HCl are summarized in Table 3. Every value is an average of three runs. As can be seen, the nature of the heteropoly acid exerts a certain effect on the degree of co-precipitation. Quantitative co-precipitation of Fr^{212} and Cs^{134} with acids containing tungsten was observed; if tungsten was replaced by molybdenum, there was a two-fold decrease in the co-precipitation degree. This may possibly be connected with different solubility of corresponding acids or with destruction of molybdenum heteropoly acids in highly concentrated hydrochloric acid solutions at the expense of enhancement of their oxidation capacity in such solutions. This problem awaits more detailed investigation.

To study the mechanism of co-precipitation of tracer quantities of caesium and francium with free acids, experiments were carried out with phosphotungstic acid in the presence of 0·5 mg of Cs^{+}, Bi^{3+} and Fe^{3+} cations. As shown by a series of runs, the presence of bismuth and ferrum cations had

no effect on the degree of precipitation. The same result was obtained on repeated precipitation of phosphotungstic acid. This evidence warrants a conclusion as to the isomorphous co-precipitation of francium and caesium with diheteropoly acids.

TABLE 3. Investigations on the degree of co-precipitation of tracer quantities of francium and caesium with diheteropoly acids

Acid	Degree of co-precipitation (%)			
	Fr^{212}	Fr^{212} +0·5 mg of CsCl	Cs^{134}	Cs^{134} +0·5 mg of CsCl
HSiW	~100	50	98	100
HPW	~100	50	98	100
HSiMo	50	40	50	90
HPMo	70	45	60	90

Most interesting are experimental results obtained in the presence of caesium. As can be seen from Table 3, caesium is precipitated quantitatively whatever the nature of the acid and this is apparently accounted for by weaker solubility of caesium salts with diheteropoly acids, as compared to free acids.

The degree of francium co-precipitation is in all cases about 50 per cent and does not depend on the nature of the acid. This fact becomes explicable only in the case when the precipitate formed represents pure caesium salt with some heteropoly acid, and francium cations in precipitate crystals are partly replaced by hydrogen ions contained in the strongly concentrated solution. The formation of pure caesium salt seems to be confirmed by the fact that under experimental conditions the ratio of molar caesium concentration to that of a corresponding diheteropoly acid is unity.

However, the results of these experiments show that there is no appreciable difference in the degree of co-precipitation of tracer quantities of francium and caesium, and consequently their co-precipitation with free diheteropoly acids cannot be used for separation of these elements. Of considerably greater interest in this respect are further investigations on the effect exerted by the presence of foreign cations on the degree of co-precipitation of francium and caesium salts with diheteropoly acids.

(b) *Co-precipitation of francium and caesium with triheteropoly acids.* Investigations on the co-precipitation of francium with triheteropoly acids are of an obvious interest. One of the authors, together with KOUŘIM[19], has recently found considerable differences in the degree of caesium and rubidium co-precipitation with phosphotungstic vanadium and silicotungstic vanadium acids from a 8·5 M nitric acid solution. In this connexion the authors have studied co-precipitation of francium with certain triheteropoly acids: phosphotungstic vanadium (HPWV), silicotungstic vanadium (HSiWV), phosphomolybdenum vanadium (HPMoV) from 11 M hydrochloric and 16 M nitric acid solutions.

Experimental technique was similar to that described in the preceding section. Experimental results are shown in Fig. 5

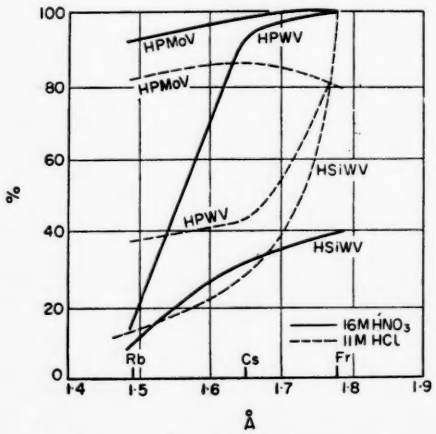

FIG. 5. Degree of co-precipitation of alkali elements with triheteropoly acids as a function of their radii.

which also includes data on caesium and rubidium.[13] These experiments made possible the estimation of co-precipitation laws as a function of true cation radii of these elements. The Fr^+ radius value is taken from YAZIMIRSKY[20].

A sharp increase in the degree of co-precipitation with increasing of cation radii was observed in both media for phosphotungstic vanadium acid. The same was

observed with silicotungstic vanadium acid in its precipitation from 11 M HCl. With phosphomolybdenum vanadium acid there is no dependence whatever on the cation radii. Of greatest interest in caesium and francium separation is the observed difference in the degree of francium and caesium co-precipitation with phosphotungstic vanadium and silicotungstic vanadium acids from 11 N HCl. The degree of francium co-precipitation exceeds that of caesium by factors 2·2 and 4, respectively. These results show the possibilities that would be opened up by works attempting to find out conditions under which these differences will increase. It will apparently be possible then to separate francium, caesium and rubidium by co-precipitating them with various triheteropoly acids.

DEVELOPMENT OF TECHNIQUES FOR CHROMATOGRAPHIC ISOLATION OF FRANCIUM FROM CAESIUM AND RUBIDIUM

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The ion-exchange chromatography method, combined with complexing, is known to be most versatile for separation of elements displaying very near chemical properties. However, complexing chromatography methods cannot be applied to separation of francium, caesium and rubidium, as these elements do not form complex anions. Available methods for caesium and rubidium separation[21–24] based on displacement chromatography making use of diluted acid solutions are very time-consuming and not always effective. This prevents their use for rapid isolation of francium from caesium and rubidium. As known from the theory of ion-exchange chromatography[25] the rate of displacement of element zones and the effectivity of their separation will increase with increasing of acid concentration in the eluting agent. Thus, in order to find out conditions for rapid and effective isolation of francium from caesium and rubidium, the authors have studied the adsorption of these elements on KU-2 and KU-1 resins from various concentrated solutions of electrolyte under static and dynamic conditions.

(1) *Determination of distribution coefficients for francium, caesium and rubidium under static conditions*

The distribution coefficient, K_d, of these elements between a sulphostyrene cation exchange resin KU-2 and electrolytic solutions of HCl, $BaCl_2$, $MgCl_2$ and NaCl of different concentrations were determined. Studies were also made of distribution coefficients for Fr, Cs and Rb between the KU-1 resin and HCl solutions of different concentrations. KU-1 is a bifunctional cation exchanger of the strongly acidic type containing two types of active groups, SO_3H and oxyphenolic OH. However, the ionic strength of the second acidic group is not considerable and it undergoes exhange only in alkali solutions. Investigations made use of tracer quantities of Fr^{212} and of 10^{-8}–10^{-6} M solutions of caesium and rubidium containing Cs^{134} and Rb^{86}. The KU-2 cation exchanger had the industrial spherical bead from of 100–150 mesh, the KU-1 exchanger was ground and the 200–250 mesh particle fraction was sorted.

Investigation techniques consisted of the following. Cation exchangers, 0·2–0·3 g, were introduced into 50 ml flasks as cations of the electrolyte studied. A corresponding electrolytic solution, 3–4 ml, was then poured into the flasks. To equilibrate the resin and the solution, samples were left to stand for 20–30 hr. Of the solution containing the alkali elements studied, 0·1 ml was then added to each sample. A comparative sample was prepared for every series of runs. It contained the same amount of element studied and of solution. The samples were shaken for 10 min by means of a shaking device. As shown by special experiments, this time is quite sufficient for reaching equilibrium. After shaking and settling of the resin, aliquots of the solution were withdrawn, dried on stainless-steel disks, and their activity was then measured.

The adsorption degree was measured by formula

$$B = \frac{A_c - A_s}{A_c} \times 100$$

TABLE 4. Degree of adsorption (per cent) of Fr, Cs and Rb on a KU-2 resin from $BaCl_2$, $MgCl_2$ and NaCl electrolytes as a function of the latter substances concentration

Electrolyte	$BaCl_2$		$MgCl_2$		NaCl	
Cations / Electrolyte concentration	Fr	Cs	Fr	Cs	Fr	Cs
0·06	67·0	62·6	72·3	70·0	84·0	83·4
0·12	59·0	54·0	65·0	62·5	77·0	73·0
0·24	45·4	37·2	55·5	50·0	65·6	60·0
0·38	—	—	—	—	52·0	48·2

TABLE 5. Degree of adsorption (per cent) of Fr, Cs and Rb on KU-1 and KU-2 resins from HCl solutions of different concentrations

M HCl	Fr (%)		Cs (%)		Rb (%)	
	KU-2	KU-1	KU-2	KU-1	KU-2	KU-1
0·6	70·0	86·0	64·3	62·0	45·5	44·6
1	55·6	—	45·5	—	34·5	—
3	37·5	44·5	23·0	38·0	15·7	27·0
6	33·0	37·0	14·9	23·0	5·6	16·0
10·5	32·6	31·3	15·0	24·5	5·9	23·4

where B is the adsorption degree (in per cent), A_c is the comparative sample activity and A_s is the activity of the sample investigated.

The distribution coefficient, K_d, is

$$K_d = \frac{B}{100 - B} \times \frac{V}{m}$$

where V is the solution volume in millilitres and m is the resin weight in grammes.

It will be noted that in the low concentration range (from tracer quantities to 10^{-3} M) the concentration of caesium has no effect on its distribution coefficient under experimental conditions.

Experimental results representing the average of five to seven runs are shown in Tables 4 and 5 and in Figs. 6 and 7. As can be seen from Table 4, the nature of Ba^{2+}, Mg^{2+} and Na^{+} cations exerts a certain influence on the degree of francium and caesium adsorption. On passing over from NaCl to $BaCl_2$ the adsorption degree will be lowered by some 20 per cent. As the electrolyte concentration is raised by a factor of 6, the degree of adsorption becomes approximately 30–40 per cent lower. There is only a slight difference in the adsorption sequence of caesium and francium, somewhat increasing with increase of the electrolyte concentration, and increasing also in the order $NaCl < MgCl_2 < BaCl_2$.

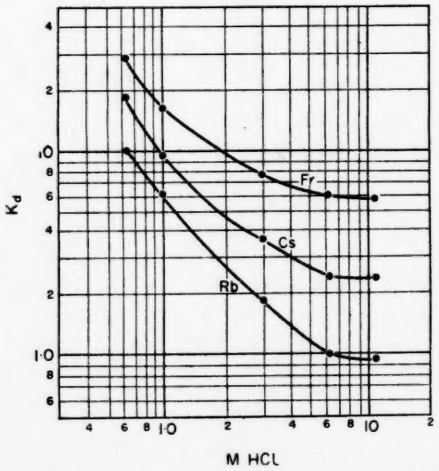

FIG. 6. Curves for distribution coefficients of Fr, Cs and Rb in KU-2 and HCl solutions as a function of the latter concentration.

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However, more interesting results were obtained in studying the adsorption of francium, caesium and rubidium cations from HCl solutions of different concentrations. As can be seen from Table 5 and Figs. 6 and 7, the adsorption on KU-2 and KU-1 cation exchangers from diluted HCl solutions decreases in the order Fr > Cs > Rb. This is accounted for by an increase, from one element to the next, in radii of their hydrated ions.

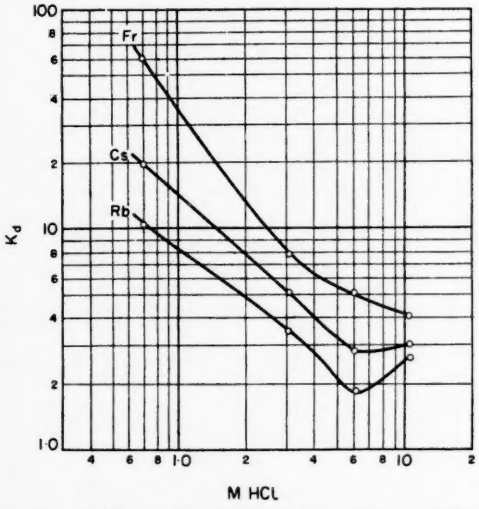

FIG. 7. Curves for distribution coefficients of Fr, Cs and Rb in KU-1 and HCl solutions as a function of the latter concentration.

With both resins approximately similar values were obtained for distribution coefficients of alkali elements in these solutions, with the exception of that for francium. The latter value in 0·6 M HCl on KU-1 is approximately twice that for KU-2.

Sharp diminishing of K_d with increase in HCl concentration to about 6 M is observed for all elements. This is in agreement with the law of mass action. With more concentrated solutions of hydrochloric acid, a constancy of K_d for all three elements was observed on KU-2. With KU-1 a gradual decrease in K_d to half its value was observed for Fr within a 3–12 M concentration range. Curves for Cs and Rb passed through a minimum at an HCl concentration of 6 M. Such a trend of curves is accounted for by the onset of another process competing with the displacing process. This is the adsorption of cations by the resin, due to increase in the cation exchange constant at the expense of cation dehydration increasing with rise in acid concentration. Thus in concentrated HCl solutions the adsorption of cations on resins will already be determined by true cation radii and K_d will increase in the order of $Fr^+ < Cs^+ < Rb^+$. However, in reality no change in the order of adsorption of these cations on KU-1 and KU-2 is observed, whereas a change takes place with a Dowex-50 resin.[26] It will be noted that a tendency for a change in the order of adsorption on KU-1 was observed with more concentrated (above 10·5 M) solutions of HCl. The observed discrepancies seem to confirm the suggestion that the chemical equilibrium concept cannot explain all phenomena taking place in ion-exchange processes on cation exchangers under equilibrium conditions. The cause of these discrepancies may lie in a different degree of change in osmotic properties of different resins, for instance in the swelling with increase in HCl concentration. This suggestion is confirmed by results, GREGOR and BREGMAN[27], where a change was observed in the order of elution of alkali elements on a highly cross-linked sulphoexchanger of a correspondingly low water content. This change will be connected here with dehydration of cations in the inner resin phase. This fact, in conjunction with results obtained by the authors, give reason to believe that internal diffusion will take place at low element concentrations as well.

The greatest difference in K_d values for neighbouring elements is observed at 5–6 M HCl. The separation factor of francium and caesium equal to their K_d ratio is 2 for KU-1 and 3 for KU-2. On the other hand, with KU-1 a considerable difference is observed for diluted solutions (~0·7 M). This warranted experiments on possible chromatographic separation of francium, caesium and rubidium on a column containing KU-2 and KU-1 resins, at above-mentioned HCl concentrations.

(2) *Studies of francium, caesium and rubidium behaviour on cation exchangers under dynamic conditions*

Experiments were conducted as follows. KU-1 and KU-2 of above-mentioned particle sizes were charged into a column 13 × 0·3 cm. Equilibrium with HCl was reached within 24 hr. After this Fr, Cs and Rb were adsorbed from a solution of 0·05–0·1 ml. Equal HCl concentrations were used in all procedures, elution included. Every drop was collected on a moving band of tracing paper and dried under an infra-red lamp. Activities were measured by a combined α, β-counter. Beta activity was measured by an end-window counter T-25 BFL (Russian mark), the mica thickness being 1·5 mg/cm², and α-activity by a scintillation counter with a ZnS crystal (Ag) and a photomultiplier FEU-19 (Russian mark). The target was placed between the two counters and measurements were made simultaneously.

Despite a considerable difference in distribution coefficients of Fr, Cs and Rb in 6 M HCl on KU-2, their separation appears to be impossible. This can be seen from the Cs and Rb elution chromatograph shown in Fig. 8. A change in the order of elution of these elements is observed. It corresponds to that observed by DIAMOND[26] and is in contradiction with the trend of K_d curves

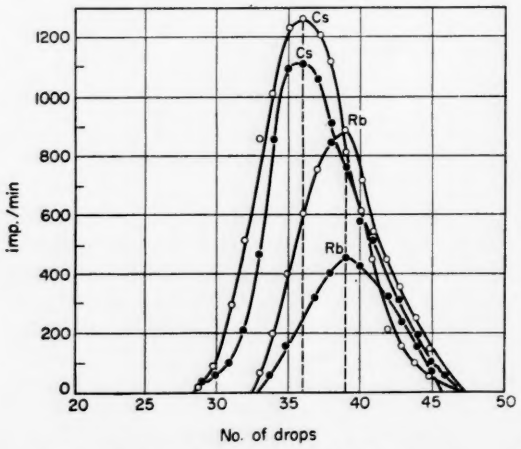

FIG. 8. Elution of Cs and Rb with 6 M HCl on the KU-2 cation exchanger. Rate, 2 drops/min.

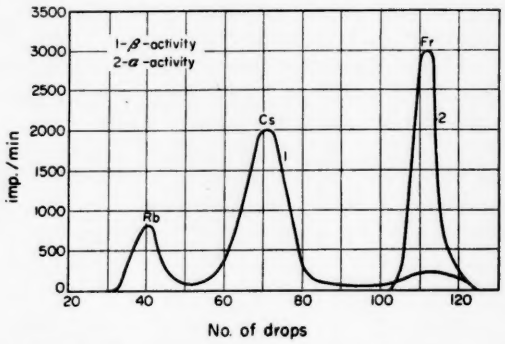

FIG. 9. Chromatograph of Fr, Cs and Rn separation from 5·5 M HCl. Rate, 3 drops in 1 min.

obtained under static conditions. This fact is a proof that distribution coefficient values determined under static conditions are absolutely insufficient for predicting the possibility of ion exchange chromatographic separation of elements. They give no insight into the dynamics of the process investigated.

This is confirmed by experimental results obtained on KU-1. Though separation factors determined under static conditions on KU-1 are slightly lower than for KU-2, nevertheless effective separation of the three elements is obtained on KU-1.[28] This can be seen from the chromatograph shown in Fig. 9. The time of separation of the three elements by means of 5·5 M HCl is 20–40 min, depending upon the solution flow velocity. The elution order for various elements on this resin corresponds to their K_d values determined under static conditions.

The separation of caesium and rubidium on KU-1 by means of 0·7 M HCl was also effective but time consuming (4–5 hr). This is in agreement with theoretical concepts of ion-exchange chromatography mentioned above. The optimum concentration of HCl required for rapid separation of heavy alkali elements francium, caesium and rubidium, on KU-1 is 5·5 M. This fact introduces new concepts in the practice of ion exchange chromatographic separation of alkali elements, according to which optimum acid concentrations in eluting agents used for separation of single-charged cations were considered to be 0·1–0·3 M.[25]

The specificity of KU-1 in rapid separation of francium, cesium and rubidium is of great interest, but its nature is not yet elucidated, and the question awaits further investigation.

Finally it may be stated that an original method for the isolation of francium, the most active metal of the Mendeleev system of elements, from its analogues, caesium and rubidium, has been first worked out as a result of conducted investigations. It permits the recovery of radiochemically pure preparations of Fr^{212} and Fr^{223}. Their application will considerably extend the domain of problems connected with studies of francium chemical properties.

DETERMINATION OF ACTINIUM CONTENT OF URANIUM MINERALS BY MEANS OF Fr^{223}

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PEREY has suggested a rapid method for determination of actinium in natural ores by the daughter Fr^{223}.[29] One of the authors of the present paper, together with KOUŘIM and FILATOVA, has studied the applicability of this method to determination of actinium in uranium ores.[30] Two hundred grammes of a uranium ore containing approximately 20 per cent of U_3O_8 were taken for investigations. Two methods were used for actinium isolation. One was based on the conventional technique of actinium isolation from ores. Another involved extraction of actinium with a solution of thenoil trifluoracetone (TTA) in benzene at pH = 3·5–5. Fr^{223} was separated from actinium upon establishment of equilibrium (in 4 hr) by co-precipitating it with free phosphotungstic acid from a concentrated solution of hydrochloric acid. The activities of isolated francium preparations were 12–15 per cent of values calculated on the assumption that, at a natural isotopic composition of uranium, Ac^{223} is in equilibrium with U^{235}. The activity observed was independent of the method of actinium isolation from the ore. A suggestion was made that actinium was adsorbed by the finely dispersed ore fraction insoluble in hot concentrated HNO_3 on multiple processing of the ore. This fraction contained 40 per cent of the ore activity.

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Caesium-137 Labelled Algae for Filtration Studies

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A method is described whereby the green algae Chlorella and Scenedesmus were cultured in a growth medium containing Cs^{137}. These radioactive algae were used as a suspension in water passing through a column of filter sand. The distributions of the algal cells retained in the filter were measured with a scintillation counter mounted externally to the column. Calibrations of the shielded scintillation counter for the amount of activity per algal cell, and for the geometry of the filter column are described.

LES ALGAE MARQUÉES DE CÉSIUM-137 POUR LES ÉTUDES SUR LA FILTRATION

On décrit une méthode par laquelle les algae vertes Chlorella et Scenedesmus furent cultivées dans un milieu contenant du Cs^{137}. Ces algae radio-actives furent employées en suspension dans l'eau qui passait à travers une colonne de sable de filtre. La mesure des distributions des cellules algales retenues dans le filtre se fit au moyen d'un compteur à scintillement monté extérieurement à la colonne. On décrit l'étalonnage du compteur à scintillement abrité pour la quantité d'activité par cellule algale, et pour la géométrie de la colonne-filtre.

ПРИМЕНЕНИЕ ВОДОРОСЛЕЙ, МЕЧЕНЫХ Cs^{137}, В ИССЛЕДОВАНИХ ПО ФИЛЬТРАЦИИ

Описан метод, в котором зеленые водоросли Chlorella и Scenedesmus культивировались на среде, содержащей Cs^{137}. Эти радиоактивные водоросли в водной суспензии пропускались через колонку, наполненную песком. Распределение клеток водорослей, остающихся на фильтре, измеряли сцинтилляционным счетчиком, расположенным вне колонки. Экранированный сцинтилляционный счетчик был градуирован в единицах активности на клетку водоросли. Описана геометрия колонки для фильтрации.

Cs^{137}-MARKIERTE ALGEN FÜR FILTERUNTERSUCHUNGEN

Eine Methode für Kulturen von grünen Algen Chlorella und Scenedesmus in Cs^{137} enthaltendem Medium wird beschrieben. Diese radioaktiven markierten Algen, suspendiert in Wasser, wurden durch eine Sandsäule filtriert. Die Verteilung der Algenzellen die im Filter zurückblieben, wurde mittels eines Szintillationszählers aussen an der Säule gemessen. Die Kalibkrierung des aggeschirmten Szintillationszählers bezüglich der Menge der Aktivität pro Algenzelle und der Geometrie der Filtersäule wird beschrieben.

INTRODUCTION

To investigate experimentally the laws governing the filtration of particles suspended in a fluid passing through a porous granular medium, a method was required to determine the distribution of the arrested particles in the column.

The particles had to be of a uniform size, discrete, of definable shape, denser than the fluid, strong enough to resist the fluid shear and one or two orders of magnitude smaller than the grains of the filter medium. For this purpose two species of green algae were

chosen, Chlorella and Scenedesmus, suspended in water filtering through sand columns with a grain size of approximately 0·5 mm.

It was decided to measure the distributions of the algae in the sand column by labelling them with a radioisotope and detecting them by an instrument mounted externally to the column. Therefore an isotope was required which:

(1) would be taken up by the algal cells during growth,
(2) would not be returned by the algae to solution in non-radioactive water,
(3) could be detected through the sand, water and glass walls of the filter column.

As culture of the algae would take a few weeks, and the harvesting, washing and experimentation an extra few days, a half-life of less than 100 days would have been undesirable.

After consideration of several alternative isotopes caesium-137 was chosen. It also had the advantage of being immediately available where the experiments were conducted.

ALGAL CULTURE AND HARVESTING

The principal algal culture was grown in a 10 l. (nominal capacity) aspirator bottle, illuminated by circular fluorescent lamps. Subsidiary cultures were grown in 500 ml measuring cylinders arranged round the 10 l. bottle. Air containing 5–10 per cent CO_2 was continuously bubbled through all the cultures. This was sufficient to keep all the algae in the measuring cylinders in suspension, but a magnetic stirrer had to be provided to agitate the 10 l. culture.

The culture medium had to support the autotrophic growth of the algae and suppress heterotrophic organisms such as moulds, bacteria and protozoa. It has been shown by WILLIAMS and SWANSON[1] that algae take up caesium and potassium in a similar manner, and in order to have a significant amount of caesium taken up by the algae the potassium in the growth medium must be reduced to a minimum. After several trials of different media the following was found to be satisfactory:

Per litre of solution		
Sodium nitrate	2·5 g	
Magnesium sulphate	4·9 g	
Potassium dihydrogen phosphate	0·25 g	
Ferric citrate	3·0 mg	
Zinc sulphate	0·4 mg	Micrometabolic constituents
Manganese sulphate	0·3 mg	
Boric acid	0·3 mg	
Cupric chloride	0·003 mg	

Caesium-137 was added as carrier-free caesium chloride, at a concentration of 100 μc/l. and sodium hydroxide was added to bring the pH between 5·0 and 6·0.

It generally took cultures 15–20 days to become a dark opaque green suspension approximately 2×10^8 algal cells/ml. Usually a 20–30-day culture was used, and the original culture was centrifuged to separate the algae. These centrifuged algae were washed in distilled water, recentrifuged and then the process repeated. Finally the algae were dispersed in a tank of tap water supplying the filter.

To test that the Cs^{137} taken up by the algae during growth was not passed back into the water (which was an indispensable requirement of the experiment) such a triple-washed suspension was shaken in distilled water in a flask for a week. The algae were then separated from the water with a millipore filter. The algae on the millipore membrane exhibited considerable radioactivity, whereas the water had no detectable activity.

EXPERIMENTAL APPARATUS

The filter consisted of a glass column containing sand, with connexions to the column for maintaining constant water flow rate, and for measuring the pressure at various points in the filter.

The radioactivity distributions were

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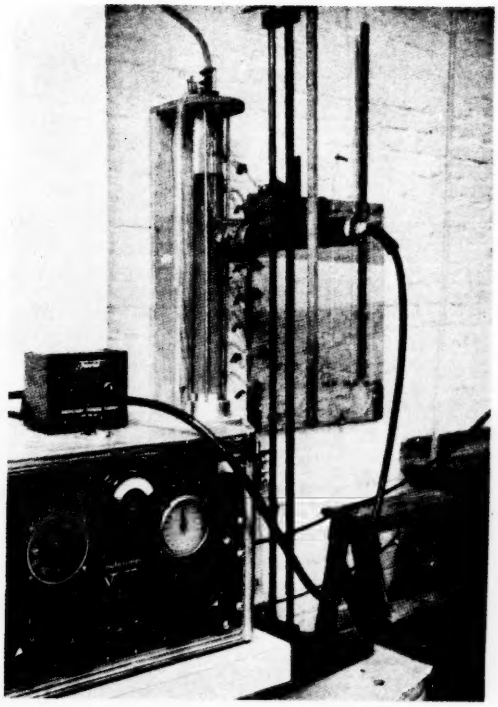

FIG. 1. Filter assembly with scintillation detector.

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measured with a lead shielded scintillation counter coupled to a timing and scaling unit. The lead shield had a horizontal slot 1 cm × 7 cm through to admit radiation from the filter to the scintillation crystal. The shielded scintillation detector and photomultiplier was mounted on a vertical rack and pinion to enable it to be set against any level of the filter. The complete assembly is shown in Fig. 1.

MEASUREMENT OF RADIOACTIVITY

To determine the distribution of the algal cells in the depth of the filter column two calibrations were required.

The first of these was to determine to what extent the count rate recorded by the scintillation counter was affected by radioactive material not exactly opposite the collimating slit in the lead shield. This characteristic of the shield and source geometry was determined by use of a plane source of Cs^{137} (CsCl solution as a thin layer in a glass container fitting inside the filter column) moving this source relative to the scintillation counter and recording the count rate. The resulting "smear" of count rate, expressed as a percentage of the maximum count rate (immediately opposite the slot) is shown on Fig. 2.

The second calibration was to determine what count rate was recorded from a known number of algal cells in the filter pores. This was achieved by taking a radioactive algal suspension in water, which had been counted in a haemocytometer, placing it in the empty filter column and then adding sand and vibrating to remove air and to consolidate the sand column. Algal cells were then trapped uniformly in the sand pores. Care was taken to leave no column of algal suspension above the sand, which might have settled on the sand surface giving a locally higher concentration of activity. By locating the counter at mid-depth, recording the count rate and correcting it for the "smear" characteristic the count rate for a known cell concentration in the pores was determined. This had to be done for each species of algae as the mean amount of activity per algal cell was different. It was assumed that the radioactivity was distributed statistically uniformly on all the algal cells, as enumerated in the haemocytometer. This microscope count also enabled an examination to be made as to whether the culture contained many dead cells or was significantly contaminated with fungi or

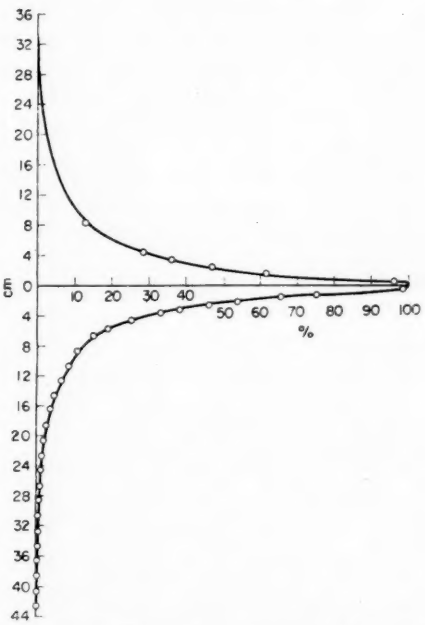

FIG. 2. Smear from plane source of Cs^{137} scintillation counter with slotted lead shield.

bacteria, which might have taken up a significant fraction of the Cs^{137}. Using the largely inorganic medium already described no significant contamination was seen and very few dead (colourless) algal cells detected. This was not true for the medium suggested by WILLIAMS and SWANSON[1] which supported dense bacterial populations, hence its use was abandoned.

COUNT RATE DISTRIBUTIONS

During a filtration experiment count rates were recorded at suitable depths of the filter column every 30 min. Due to the nature of the filtration process it was necessary to take count rates at every centimetre depth for the first 5 cm, then at 7 cm, 10 cm and below that at 5 cm intervals.

Such a count rate distribution is shown as curve 1 on Fig. 3. This curve had to be corrected for the activity of algae collecting on the surface of the sand column, giving a corrected curve 3. This curve was the result of some true distribution, curve 4, being "smeared" by the characteristic (given on Fig. 2) of the counter assembly. There is no known analytical method of taking the smeared distribution curve 3 and applying the counter characteristic, Fig. 2, to it to derive the true curve. The method used by the author was to assume a trial distribution and "smear" it with the counter characteristics to see if the resulting distribution matched curve 3. Successive approximation enabled the true distribution to be found, but the numerical computation of such a method is extremely tedious. A sample analysis is shown in Table 1.

From a numerical analysis the curve 4 was

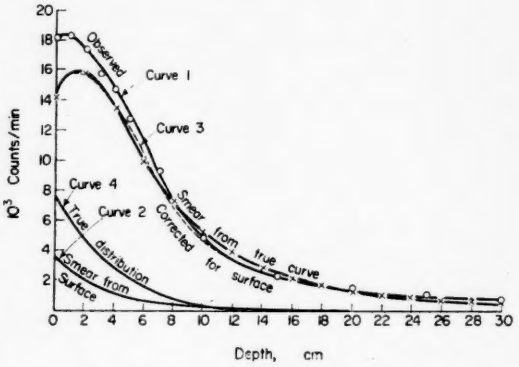

FIG. 3. Count rate distribution curves.

obtained which produced the effect of curve 5, almost identical with the corrected experimental curve 3. This indicated that curve 4 was the true distribution of count rate through the filter depth. From a previous calibration the count rates of curve 4 were translated to algal cell concentrations in the filter pores. This procedure had to be repeated for every distribution recorded as the filter run proceeded. A more effective shield to the counter with better collimation would have reduced this burden of analysis.

TABLE 1. Tabular method of determining "smeared" curve of count rate, from trial "true" distribution and known counter "smear" characteristics. (Approximately 1/7th of the full table shown).

Depth (cm)	0·21	0·28	0·38	0·53	0·76	1·0	0·76	0·53	0·38	0·28	0·21	Counter "smear"
1						400	304	212	152	112	84	
2					228	300	228	159	114	84	63	
3				119	171	225	171	119	85	63	47	
4			64	90	128	169	128	90	64	47	35	
5		35	48	67	96	127	96	67	48	35	27	
6	20	27	36	50	72	95	72	50	36	27	20	
7	15	20	27	38	54	71	54	38	27	20	15	
8	11	15	20	28	40	53	40	28	20	15	11	
9	8	11	15	21	30	40	30	21	15	11	8	
10	6	8	11	16	23	30	23	16	11	8	6	
11	5	6	9	12	17	23	17	12	9	6	5	
12	4	5	6	9	13	17	13	9	6	5	4	
13	3	4	5	7	10	13	10	7	5	4	3	

Observed ("smeared") value is diagonal sum (e.g. 9 cm value).

"True" distribution.

Any value is product of "smear" value and "true" value e.g. $23 \times 0{\cdot}76 = 17$.

STUDY OF FILTRATION

With the algal deposit concentrations measured for known depth and time coordinates the mathematical and hydrodynamic laws of filtration were studied.

Previously only one complete statement of the space–time distribution of deposited material in a homogeneous filter had been made.[2] This has been found to be inadequate in various respects and an alternative formulation has been proposed by Ives[3]. This is

$$\frac{\partial\sigma}{\partial t} = v\left(\lambda + c\sigma - \frac{\phi\sigma^2}{f-\sigma}\right) C \qquad (1)$$

where

σ = storage ratio = $\dfrac{\text{volume of deposit}}{\text{unit volume of filter}}$

t = time

v = approach velocity of water to filter surface

λ, c, ϕ = rate factor parameters, characteristic of the suspension, state of flow and filter grains

f = filter initial porosity

C = volume concentration of suspension in the flow.

The volume concentration of suspension in the flow and the storage ratio are linked by the continuity equation

$$\frac{\partial\sigma}{\partial t} + v\frac{\partial C}{\partial x} = 0 \qquad (2)$$

where x is the depth in the filter measured from the filter surface.

The algal deposit concentrations measured by the technique described enable graphs of σ against t to be plotted for each interval of depth. Hence $\partial\sigma/\partial t$ is the slope of such a graph.

Putting

$$y = \lambda + c\sigma - \frac{\phi\sigma^2}{f-\sigma} \qquad (3)$$

then from (1)

$$y = \frac{\partial\sigma/\partial t}{vC}.$$

For the top layer of the filter $C = C_0$, the inflow concentration, so y can be evaluated for various values of σ from the σ against t graph. A plot of y against σ will enable the constants λ, c and ϕ to be evaluated from equation (3). With these specified, it is possible to derive the deposit in the filter, and the concentration in the flow through the filter for any depth and for any time, from equations (1) and (2). In fact no analytical solution is known for these equations, so they have been solved numerically by finite difference methods on an electronic digital computer.

Details of this, and the analysis of pressure loss through the filter layers is contained in the author's paper to the *Institution of Civil Engineers*.[3]

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A Method of Leak Testing Hermetically Sealed Components Utilizing Radioactive Gas

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A method of leak testing hermetically sealed components such as transistors, relays, frequency standard crystals, small munitions, etc., utilizing a chemically inert radioactive gas (krypton-85) is described. A leak rate formula based on Poiseuille's law is developed and the limitations in measurement imposed by the range of validity of this formula and of the random nature of radioactive decay is discussed. Means for differentiating between radioactive gas which has leaked inside the part being tested and gas absorbed on its surface is presented. A logarithmic rate unit called the leak index is proposed. A brief description of industrial equipment for accomplishing leak rate measurements along with precautions to assure full safety in its operation is given.

UNE MÉTHODE POUR LA RECHERCHE DES FUITES DANS LES CONSTITUANTS HERMÉTIQUEMENT ENFERMÉS EN EMPLOYANT UN GAZ RADIOACTIF

On décrit une méthode pour éprouver contre les fuites les constituants enfermés hermétiquement, tels que les transisteurs, les relais, les cristaux étalons de fréquence, les petites munitions de guerre, qui se sert d'un gaz radioactif et inerte du pointe de vu chimique (le krypton-85). On développe une formule pour le taux de fuite basée sur la loi de Poiseuilleet on discute les limitations dans la mesure qu'impose la rangée de validité de cette formule et le hasard compris dans la nature de la décadence radioactive. On présente le moyen pour reconnaître du gaz radioactif qui est entré dans le sujet mis à l'essai le gaz absorbé sur sa surface. On propose un indice de taux logarithmique, l'indice de fuite. On décrit brièvement l'installation industrielle destinée à achever les mesures du taux de fuite, ainsi que les précautions qui assurent la sécurité totale au cours de son fonctionnement.

МЕТОД ИСПЫТАНИЯ НА УТЕЧКУ ГЕРМЕТИЧЕСКИ ЗАПАЯННЫХ УСТРОЙСТВ, СОДЕРЖАЩИХ РАДИОАКТИВНЫЙ ГАЗ

Описан метод испытания на утечку герметически запаянных устройств, как например транзисторов, реле, кристаллических эталонов частоты и проч., содержащих химически инертный радиоактивный газ (криптон-85). Из закона Пуазеля выведено уравнение для скорости утечки и рассматриваются пределы возможных измерений, обусловленные применимостью уравнения и природой радиоактивного распада. Приводится методика. позволяющая отличать радиоактивный газ, проникнувший внутрь испываемого устройства, от газа, адсорбированного на поверхности. Предложена логарифмическая единица скорости, названная индексом утечки. Дается краткое описание промышленного оборудовани для измерений скорости утечки, а также приводятся меры предосторожности, обеспечивающие полную безопасность персонала.

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EINE METHODE ZUR AUFFINDUNG VON LECKS IN HERMETISCH ABGESCHLOSSENEN TEILEN MIT HILFE EINES RADIOAKTIVEN GASES

Eine Leckprüfmethode von hermetisch abgeschlossenen Bestandteilen wie z.B. Transistoren, Relais, als Frequenzstandards verwendete Kristalle, kleinkalibriger Munition mit Hilfe eines chemisch inerten radioaktiven Gases (Krypton-85) wird beschrieben. Ausgehend vom Poiseuille'schen Gesetz wird eine Formel für die durch Lecks pro Zeiteinheit ausströmenden Mengen abgeleitet, und es werden die durch den Gültigkeitsbereich dieser Formel und durch den Zufälligkeitscharakter des radioaktiven Zerfalles bedingten Grenzen bei der Messung diskutiert. Unterscheidungsmöglichkeiten zwischen dem Gas, das indas Innere des geprüften Teiles durch Lecks eingedrungen ist und dem an seiner Oberfläche absorbierten, werden aufgezeigt. Eine logarithmische Masseinheit, genannt "Leck-Index" wird vorgeschlagen. Die industrielle Ausrüstung zur Ausführung von Messungen der aus Lecks ausströmenden Mengen zusammen mit Vorsichtsmassnahmen, um die volle Betriebssicherheit zu garantieren, wird kurz beschrieben.

INTRODUCTION

RAPID nondestructive methods for the detection of leaks in hermetically sealed containers are presently becoming of great industrial and military importance. The probable operational reliability of many devices, such as sealed transistors, relays and munitions, is greatly reduced if a sufficiently large leak exists. Breathing with attendant introduction of water vapor or leakage of a special composition of internal atmosphere or loss of pressure or vacuum are common causes of malfunction. Various methods have been attempted in the past for leak testing. Tests, such as bubble tests, are useful for detecting large enough leaks, but usually they are very insensitive to a range of smaller leaks affecting operational reliability. Sometimes helium gas can be put in the container and a leak detected by a mass spectrometer device. In general, it would be uneconomical to tubulate large numbers of parts for mass spectrometer leak tests and then seal off the tubulature. Furthermore, this latter seal would not be tested in this procedure.

The idea has occurred to quite a few individuals that, in principle, much greater sensitivity can be obtained if completed hermetically sealed units were to be subjected to external pressure of a fluid (gas or liquid) containing a γ-ray-emitting radioisotope. Radioactivity would then be introduced within leaky containers. After suitable washing or decontamination of the outside of the containers, the gamma radiation from the inside of the leakers could be measured by a suitably sensitive radiation detector placed near the part. As is usually the case the translation of this basic idea to a practical inspection system was beset with unexpected difficulties and development problems.* The application of this procedure is at the present time expanding with great rapidity.

The availability of radioactive Kr^{85} in copious supply simplified many of the original problems connected with the chemical reactivity of other radioactive tracers that were tried at that time. An attempt to use methyl iodide tagged with radioactive iodine-131 had some degree of usefulness, but it is catalytically decomposed by, or directly reacts with, some materials. Krypton gas is, as is well known, completely chemically inert and, thereby, combines with no material used in the tested components. Radioactive Kr^{85}, due to its chemical inertness, does not participate in any metabolic processes in the body, if inhaled or ingested in any way. If accidentally inhaled for a short time, normal breathing of noncontaminated air will rapidly remove the krypton from the lungs and body tissue into which it might have diffused. With an adequate ventilating system, proper gamma-ray shielding of storage tanks and reasonable care, Kr^{85} can be handled with negligible risk to the operators. The problems of health safety will be further considered below.

* The first industrial application was made in 1954 under the guidance of Mr. C. W. Reed of the Reed–Curtis Instrument Company, the predecessor company of the Nuclear Division of American Electronics, Inc.

THEORY

Krypton-85 has a half-life of 10.3 years, so that it can be used over and over again if it does not become too diluted with air or is lost into the atmosphere. Over 99 per cent of the disintegrations give no gamma rays but emit beta rays with a maximum energy of 0.67 MeV. Only 0.7 per cent of the disintegrations give 0.54 MeV gamma rays. The primary usefulness of Kr^{85} for leak detection is dependent on this small proportion of gamma emitting disintegrations, reinforced in some applications by the emission of low-energy "bremsstrahlung". The rate of disintegration $\left(-\frac{dN}{dt}\right)$ is related to the number of atoms (N) of Kr^{85} as

$$-\frac{dN}{dt} = \frac{0.693}{t_{\frac{1}{2}}} N.$$

The half-life ($t_{\frac{1}{2}}$) of 10.3 years is equivalent to 3.25×10^8 sec. Therefore, 1 cm^3 of pure Kr^{85} at normal pressure and temperature containing 2.7×10^{16} atoms will produce total disintegrations at the rate of 5.78×10^{10}/sec which is equivalent to a maximum activity of 1.56 c/cm^3. Only 0.7 per cent of these 5.78×10^{10} disintegrations/sec or 4×10^8/sec yield gamma quanta. "Krypton-85" received from Oak Ridge contains 5 per cent of the radioactive isotope, thereby having an activity about 0.078 c/cm^3. This gas is usually diluted with air or by another gas for two reasons. One is to give the gas the effective viscosity of air. The other is to get sufficient volume for filling dead spaces in pressurized containers.

It has become customary to express leak rates in terms of standard cubic centimeters per second leaking from 1 atm pressure to a vacuum. If tests were actually made with these limitations of external and internal pressures on evacuated parts, then, at best (ignoring contributions of "bremsstrahlung") using pure Kr^{85} if such was available, a leak of $2.5 \times 10^{-9} cm^3$/sec would give only one 0.54 MeV gamma quanta per second emission for each second the part was exposed externally to the pure Kr^{85}. This theoretically limiting sensitivity per 1 sec pressure exposure is greatly reduced by the dilution with air or nitrogen. However, the effects of dilution are easily offset by properly increasing testing pressure and testing time. Since the amount of leaked-in activity increases proportionally with time, the period of exposure is often extended to many hours. A typical value for the external pressure of the radioactive gas is about 7 atm, and for an evacuated part, if a leak follows Poiseuille's law, the rate at which activity gets into the part will increase as the square of the pressure. In general, for a nonevacuated part, the ideal Poiseuille mass flow rate (Q) is given by:

$$Q = \frac{Ca^4}{8\eta L} (P_e^2 - P_i^2)$$

where L is the length and a the radius of an equivalent capillary leak channel, η is the viscosity of the gas, C is a dimensionless constant, P_e is the external pressure and P_i the internal pressure, both in atmospheres. Although all types of leaks cannot be expressed in terms of an equivalent Poiseuille capillary leak, the above type of variation of leak rate (Q) with P_e is used in practice. In certain cases, especially with small leaks, some arbitrariness is introduced when reducing measurements obtained from actually used values of P_e and P_i to standard leak rates, as presumably would be measured if $P_e = 1$ atm and $P_i = 0$. On the assumption that the radius and length of the equivalent capillary leak, and the gas viscosity (η) are all constants during the tests, then the standard leak rate (R) is related to the measured Q in units of standard cubic centimeters per second, as

$$R = \frac{Q}{P_e^2 - P_i^2}.$$

The various constants in the Poiseuille formula cancel out in the ratio of R to Q. If P_i is one and P_e is large enough compared with one, the sensitivity of the test increases approximately as the square of the external pressure. The sensitivity will be increased by a factor of 100 at about 150 lb/in^2

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testing pressure. By utilizing suitable pressures and pressure exposure times, and assuming that Poiseuille flow holds (a doubtful assumption for the smaller leaks), leaks of the order of 10^{-13} standard cm^3/sec could be detected under favourable conditions. This leak rate is so extremely small that it would take about 100,000 years for 1 cm^3 to leak from atmospheric pressure into a vacuum.

For fixed testing pressures and fixed exposure times, the sensitivity bottleneck is the efficiency of radiation detection, assuming no external surface adsorption of the gas on paints, grease, dirt or organic materials. Small parts can be counted in a well- or tunnel-like thallium activated sodium iodide crystal scintillation counter. Under practical favorable conditions, about half of the emitted gamma quanta will yield counts. The counts are random in time and are subject to Poisson statistics in the distribution of counts in a given time interval or time for a given number of counts. If the background counting rate is small compared with the part counting rate, the standard deviation of a distribution of repeated counts per unit time with an average over the distribution of N counts per unit time will be $\sqrt{N}$. Thus, the total number of counts must be increased four times to double the counting accuracy, and 100 times to increase the accuracy by a factor of 10. The scintillation crystal must be well shielded from low-level ambient radiation to reduce the background count. If the ratio of counting rate to background rate is r, the statistical inaccuracy $(\sqrt{N})$ must be multiplied by a factor F where

$$F = \frac{\sqrt{r(r+1)}}{(r-1)};$$

$F = 2.45$ for $r = 2$, $\quad 3.86$ for $r = 1.5$.

Fortunately, high precision counting is not necessary for most leak measurements. Leak rate distribution can cover a range of so many powers of 10 that even a factor of 2 or 3 makes very little practical difference in their classification. In order to emphasize this situation and incidentally to simplify typography, it is here proposed to describe leaks in terms of a "leak index" defined as minus the decimal logarithm of the standard leak rate. This is quite analogous to the universal practice of describing hydrogen ion concentration by pH. For example, a leak rate of 10^{-11} will have a leak index of 11, one of 2×10^{-11}, a leak index of 10.7, 3×10^{-11} of 10.5, 4×10^{-11} of 10.4, 5×10^{-11} of 10.3, 6×10^{-11} of 10.2, 7×10^{-11} of 10.15, 8×10^{-11} of 10.1, 9×10^{-11} of 10.05 and 10^{-10} of 10.0. Usually, accuracy of one decimal place in the logarithm will be quite adequate. If the output of a ratemeter from the scintillation counter were logarithmically attenuated, the proper classification of certain broad ranges of leakers would be greatly facilitated.

Some items to be leak tested have adsorptive surfaces such as organic coatings, or small areas of organic insulation or gasketing. Many organic materials will take up Kr^{85} under pressure and will hold it for various lengths of time after the pressure is released. The gamma radiation emitted by this adsorbed gas could make the item appear to be a leaker when, in fact, it was not.

Routine check of rejected parts with a thin window G.M. tube consistently reveals surface contaminated parts. Comparison of such rejected parts with acceptable parts of the same surface composition can be used to determine the significance, if any, of the surface contamination. Those parts with significant contamination can often be decontaminated with a brief exposure to heat. Frequently, such a heating cycle is routinely incorporated into the testing procedure of certain parts having organic coatings.

Occasionally components with very large, or so-called "gross leaks," tend to slip through the leak test as acceptable. This is due to rapid escape of the radioactive gas through the large opening during the final "pump down" phase of the leak test cycle. This does not occur, in practice, if the component contains any organic or other adsorptive material such as relay coils. In the absence of such internal adsorptive material, it is sometimes necessary to retain a slight partial pressure of Kr in the pressurizing tank before its removal for counting.

Other methods of detecting "gross leakers" such as pre-pressurization with organic liquid are being developed for special applications.

EQUIPMENT

Figs. 1 and 2 show an industrial testing unit. The activation unit includes a storage tank for radioactive gas, an activation or pressurization tank, and the vacuum pumps, compressor and other components necessary to accomplish the testing cycles. The activation unit also contains automatically programmed electronic circuitry to assure the protection of personnel from radiation hazards resulting from malfunctioning or maloperation of the equipment.

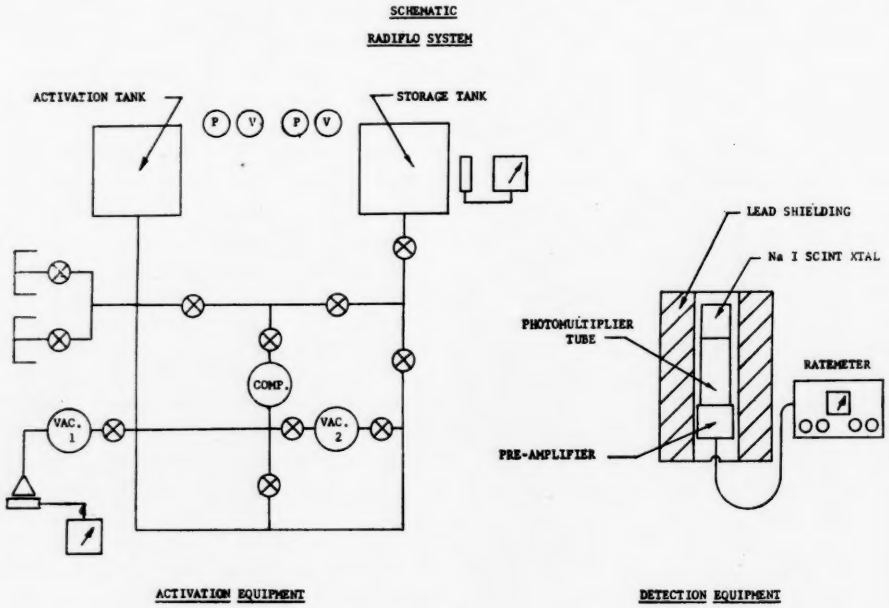

FIG. 1.

Parts to be tested are placed into the activation tank which is sealed by means of a locking ring. To prevent dilution of the radioactive Kr, the activation tank is evacuated to approximately 2 mm Hg. The air being evacuated is directed into an exhaust duct and vented to the atmosphere by means of a continuously operating blower unit. The activation tank is then pressurized to the desired level with Kr^{85}.

The activation tank remains pressurized for a pre-set length of time determined by the desired sensitivity of the test. At the conclusion of the activation cycle, the testing gas is returned to the storage tank reducing pressure in the activating tank to 2 mm of Hg absolute or less. The unit is then flushed with air to remove any residual Kr.

Because a radioactive isotope is used in this process, certain precautions have to be taken to maintain safe operation of the equipment. Various components of the activation unit are lead shielded to ensure the fact that the level of gamma radiation from the equipment is always well within the maximum permissible exposure level established by the AEC. The entire cycle is automatically programmed. A system of interlocks is incorporated in the equipment which prevents an accidental discharge of radioactive gas.

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FIG. 2.

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In conclusion, the problems of counting tested components vary tremendously depending on the characteristics such as size, presence or lack of organic material on the surface, and other incidental factors. It would not be practical to discuss all these variations at this time. Small parts can usually be counted in a well-type sodium iodide scintillation counter for gamma-ray activity and by a thin window G.M. tube for surface beta-ray activity. Larger parts are gamma counted with less efficiency than those that can be put in a well counter. Future developments in increasing counting sensitivity would enable an over-all increase in testing sensitivity or a decrease in the pressurization time necessary.

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Polyethylene-Ferrous-Ion Dosimeter for Hydrocarbon Systems in Radiation Chemistry*

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(*Received* 9 *May* 1960)

A procedure for accurately determining the total energy input into an organic system has been evaluated. The study was performed in the low-energy region of the X-ray spectrum (below 50 keV). This method eliminates the uncertainties encountered in the use of electron density ratios.

UN DOSIMÈTRE À POLYÉTHYLÈNE-ION-FERREUX POUR LES SYSTÈMES D'HYDROCARBURES DANS LA CHIMIE DU RAYONNEMENT

On a évalué un procédé pour la mesure exacte de l'énergie totale entrant dans un système organique. On a fait l'étude dans la région à basse énergie du spectre de rayons-X (moins de 50 keV). Par cette méthode on évite les incertitudes qui se trouvent à l'emploi des rapports de la densité d'électrons.

ПОЛИЭТИЛЕН-Fe^{++} ДОЗИМЕТР ДЛЯ УГЛЕВОДОРОДНЫХ СИСТЕМ В РАДИАЦИОННОЙ ХИМИИ

Производится оценка метода точного определения общего количества энергии, сообщаемой органической системе. Исследования производились в области низких энергий рентгеновского спектра (ниже 50 кэв). Этот метод позволяет избежать неопределенности, возникающей иногда при использовании коэффициентов электронной плотности.

POLYÄTHYLEN- FERRO-IONEN-DOSIMETER FÜR KOHLENWASSERSTOFF-SYSTEME IN DER STRAHLENCHEMIE

Ein Verfahren zur genauen Bestimmung der totalen Energieabgabe an ein organisches System wurde ausgewertet. Die Untersuchung wurde im niederenergetischen Teil des Röntgen Spektrums (unter 50 keV) ausgeführt. Diese Methode vermindert Ungenauigkeiten, welche durch Anwendung von Elektronendichte Verhältnissen auftreten.

In the course of studies under way on the irradiation of hydrocarbon systems with low energy X-rays (effective energy of 20 keV) from a Machlett OEG-60 beryllium window tube operating at 50 Kvp and 45 MA, one phase of the work which presented considerable difficulty was that of determining the total energy absorbed by the system. Since the spectrum is a continuous one, it is not feasible to use attenuation coefficients for a direct conversion from a dosimeter system to a sample system.

The procedure which has been used previously involves the ferrous ion dosimeter and electron density ratios. In this method one converts the volume of the hydrocarbon

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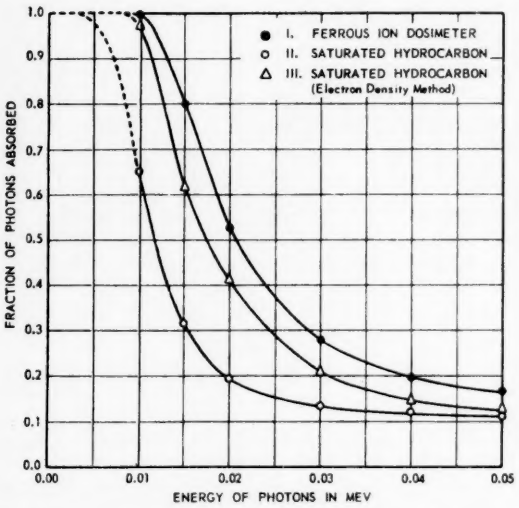
I. FERROUS ION DOSIMETER
II. SATURATED HYDROCARBON
III. SATURATED HYDROCARBON (Electron Density Method)
FRACTION OF PHOTONS ABSORBED
ENERGY OF PHOTONS IN MEV

FIG. 1. Comparison of the photons absorbed as calculated by the electron density method and the attenuation coefficient method.

system to an equivalent volume of dosimeter solution by the use of the ratio of the electron densities of the two systems. The energy absorbed by the equivalent volume of dosimeter solution is then measured expermentally.

To test the reliability of this method, calculations of photon absorption at various energies were made for a 30 ml dosimeter solution (0.01 N ferrous iron, 0.8 N sulfuric acid) and a 30 ml hydrocarbon system (iso-octane) with attenuation coefficients obtained from NBS Circular 583.‡ These data are contained in Fig. 1, Curves I and II. The electron density method is represented by Curve III in Fig. 1. This curve was calculated by multiplying the volume of the hydrocarbon system (30 ml of iso-octane) by the electron density ratio (0.713) to obtain an equivalent volume of dosimeter solution (21.39). Appropriate attenuation coefficients were then used to determine the fraction of photons absorbed. The magnitude of the difference between curves II and III clearly indicates that the electron density ratio should not be used in this region of the spectrum.

In order to minimize errors associated with dosimetry measurements, it is best to make all energy measurements on as nearly the same system as possible. The electron density ratio correction has been a source of constant concern; therefore, a dosimeter system which has the same atomic components as a hydrocarbon system has been evaluated. This method involves placing a polyethylene disc between the X-ray tube and the ferrous ion dosimeter. Thus, by a direct measurement of milliequivalents of ferrous iron oxidized with and without the polyethylene in place, the energy absorbed by the polyethylene can be determined. This

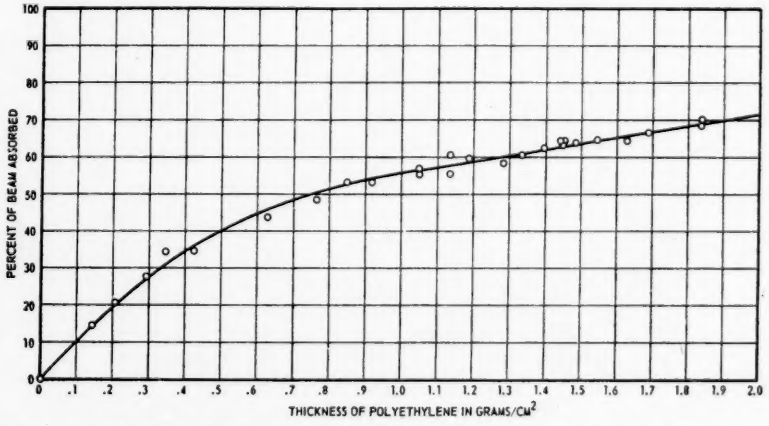

FIG. 2. Calibration curve for "polyethylene–ferrous-ion dosimeter".

‡ GRODSTEIN G. W. *J. Res. Nat. Bur. Stand.* Circ. No. 583 (April 1957).

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is taken to be the energy absorbed by a hydrocarbon system which presents the same number of milligrams per square centimeter to the X-ray beam. Fig. 2 is a calibration of a Machlett OEG-60 X-ray tube for per cent of total beam absorbed as a function of polyethylene thickness in mg/cm². From this curve one reads the fraction of the beam absorbed by the sample. The energy absorbed is obtained by multiplying this fraction by the total energy output of the X-ray beam.

The "polyethylene–ferrous-ion dosimetry" will aid in the evaluation of radiation chemistry studies of hydrocarbons when low-energy X-rays are the ionizing radiation. Also, this dosimetry technique can be adapted to other types of radiation chemistry studies which involve only a change in energy range from the above indicated region.

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Identification of Gamma Emitters Formed by Neutron Activation Including Tables of Radionuclides Formed by Neutron Capture

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Gamma-emitting nuclides formed by neutron capture (and some other neutron reactions) can be identified by measuring the half-life and gamma energy preferably against a standard which might be the nuclide suspected. The uncertainty of these two properties is used to form an uncertainty rectangle around a point on a map with the half-life on one axis and gamma energy on the other. Maps are given of neutron-formed gamma-emitting nuclides (except fission products) as listed in the STROMINGER–HOLLANDER–SEABORG tables to facilitate such identification work which may be met in any radiochemical procedure, activation analysis, reactor product contamination and other work.

IDENTIFICATION DES ÉMETTEURS GAMMA FORMÉS PAR L'ACTIVATION NEUTRONIQUE; Y COMPRIS DES TABLEAUX DE RADIONUCLÉIDES FORMÉS PAR LA CAPTURE DE NEUTRONS

Les nucléides émetteurs de gamma formés par la capture de neutrons (et par quelques autres réactions neutroniques) peuvent s'identifier par la mesure de la période de demi-valeur et de l'énergie gamma, de préférence contre un étalon qui pourrait être le nucléide attendu. L'incertitude de ces deux caractéristiques sert à former un rectangle d'incertitude autour d'un point sur une carte ayant la période de demi-valeur sur un axe et l'énergie gamma sur l'autre. On présente des cartes de nucléides, émetteurs de gamma, produits par des neutrons (sauf les produits de fission) tels que les cataloguent les tableaux STROMINGER-HOLLANDER-SEABORG, afin de faciliter la tâche d'identification que l'on peut rencontrer en aucun procédé radiochimique, à la suite de l'analyse par activation, de la contamination par les produits d'un réacteur et au cours d'autre travail.

ИДЕНТИФИКАЦИЯ ГАММА-ИЗЛУЧАТЕЛЕЙ, ПОЛУЧАЮЩИХСЯ ПРИ ОБЛУЧЕНИИ НЕЙТРОНАМИ, И ТАБЛИЦЫ РАДИОАКТИВНЫХ ЯДЕР, ОБРАЗОВАННЫХ ПУТЕМ ЗАХВАТА НЕЙТРОНОВ

Гамма-излучатели, образованные при захвате нейтронов (или по какой-либо другой нейтронной реакции) могут быть идентифицированы при помощи измерения периода полураспада и энергии гамма-лучей предпчтительно с применением эталона, которым может служить искомый изотоп. Неопределенность в этих двух свойствах использована для графического изображения величины разброса в координатах: период полураспада-энергия гамма лучей. Даны графики для входящих в таблицы Штромингера-Холлэндера-Сиборга гамма-излучателей, образованных нейтронами (за исключением продуктов деления). Эти графики облегчают работу по идентификации ядер при применении радиохимической методики активационного анализа при определении степени загрязнения продуктов в реакторе и т.п.

DIE IDENTIFIZIERUNG VON γ-STRAHLEN, DIE DURCH NEUTRONEN-AKTIVIERUNG HERGESTELLT WURDE, MIT HILFE VON TABELLEN VON RADIONUKLIDEN AUS DEM NEUTRONEN-EINFANG-PROZESS

γ-strahlende Nuklide, die durch Neutronen-Einfang, oder durch andere Neutronenreaktionen gebildet werden, lassen sich durch Messung von Halbwertszeit und γ-Energie identi-

fizieren, besonders wenn dazu ein Vergleichs-Standard des vermuteten Nuklides benützt wird. Die Unischerheit dieser beiden Eigenschaften wird zur Zeichnung eines Unsicherheits-Rechteckes rund um einen Punkt in einem Halbwertszeit-γ-Energie-Diagramm verwendet. Solche Diagramme werden für γ-Strahler aus Neutronenreaktionen (mit Ausnahme von Spaltprodukten) angegeben, deren Daten den STROMINGER-HOLLANDER-SEABORG-Tabellen entnommen sind. Sie dienen der Vereinfachung der Identifizierung bei radiochemischen Prozessen, Aktivierungs-Analysen, Verseuchungen mit Reaktor-Produkten und ähnlichen Untersuchungen.

INTRODUCTION

WHEN a piece of matter is exposed in a nuclear reactor, different types of neutron reactions and other less common reactions (e.g. photo-nuclear reactions and secondary nuclear reactions) occur. In a lot of practical cases several radioactive nuclides are formed in neutron-exposed matter. The reason may be that the bulk element contains more than one isotope, that more than one element in macro content is present or that microcomponents are present. Thus one meets the problem of identifying different activities. This is the case in many practical cases, e.g. activation of matter to get radioactive tracers or radiation sources, in samples from radiochemical separations, in activation analysis, in studying induced radioactivity in reactor materials, such as coolants and construction materials, in studying contamination generally or in the special case of reactor corrosion products or leaks, etc.

The mode of identification can be made in several ways and different workers certainly have their own habits. For some years we have found it useful, when dealing with gamma emitters formed by reactor exposure, to use a chart showing the half-life on one axis and gamma energy on the other. In order to identify a certain activity, these properties have to be determined with some accuracy. When this is done the relevant place on the chart is found and then the certainty of the identification can be discussed. The procedure will be discussed below and some examples given.

GAMMA-ENERGY DETERMINATION

It may be stated that the determination of gamma-ray energies is at present made in a most practical way with the scintillation method when moderate accuracy (magnitude per cent) is sufficient. A NaI(Tl) crystal and a single- or multi-channel analyser will serve this purpose. Of course every instrumental method requires its special considerations with regard to source strength, geometry, mode of operation, etc., in order to get optimum results from it. Such details lie, however, outside the scope of this paper. We shall only assume that the gamma energy has been determined in some manner together with some measure of its accuracy. A very useful collection of gamma scintillation spectra has been issued by HEATH[4] and may be very useful in connexion with work to be described below.

The practical determination is often got from a comparison with standard lines. In many cases one might have a suspicion of what constitutes the unidentified activity. In this case a standard sample of the element in question will serve for a comparison. In activation analysis or in problems of induced activities it is usual to activate standard samples of certain elements together with the sample to be studied.

HALF-LIFE DETERMINATIONS

The half-life can often be studied in the gamma scintillation spectrometer in connexion with gamma-energy studies. A practical condition is that it is not too long.

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In many cases the half-life has to be studied by taking spectra at different times. The apparatus has then to be stable enough. A direct comparison with standard samples, however, simplifies the determination. Especially this is the case when we expect the presence of a certain element and are able to compare it with a standard sample.

The two half-lives to be compared should, for best accuracy, be as close as possible. In this case we can compare the sample and the standard at different times after activation. The comparison can be made in several ways. In a gamma scintillation spectrum the area or the height of a photo peak may be evaluated (after appropriate background corrections which often is the main problem) and compared with the same property (A_o) of the standard.

If A is the intensity property of the sample, we have

$$A = A_o e^{-\lambda t} \tag{1a}$$

$$A_s = A_{os} e^{-\lambda_s t}. \tag{1b}$$

Further

$$\frac{A}{A_s} = \frac{A_o}{A_{os}} e^{-(\lambda - \lambda_s)t}. \tag{2}$$

The activity ratio is normalized so that it is exactly one at some time, e.g. at the first instance of comparison. Thus

$$\kappa = e^{-\Delta\lambda t} \tag{2a}$$

where $\Delta\lambda = \lambda - \lambda_s$.

κ is now evaluated at different times. If it is possible, it should be studied for several half-lives because κ will sensibly differ from one in that case. If the two activities are identical, the accuracy of the decay constant determinations is of course better the longer the decay time (up to some optimum value). It can be shown that, provided κ is close to one,

$$\Delta\kappa = \kappa - 1 = -\Delta\lambda t.$$

If κ is invariantly equal to one within some experimental uncertainty, the half-life is identical to that of the standard with a corresponding uncertainty which can be calculated from the relations given. If several activities contribute to the activity studied, the κ–t diagram will show corresponding systematic departures, i.e. show a gradual (exponential) decay or rise to a constant level. In fortunate cases the decay constant of the disturbing activity can be measured from the kinetics but in most cases hitherto treated simple identifications have been the object. A special point of the procedure outlined is that only quotients are measured and thus one eliminates to a certain extent drift of the detection apparatus and it is possible with some care to move the samples to closer positions with regard to the detector during decay.

NOTE ON ACTIVATION ANALYTICAL DETERMINATIONS

It might be remarked that the procedure described by equations (2) and (2a) is equivalent to the determination by activation analysis of an unknown component. The subsequent recording of spectra or counting in a certain energy region on different instances is used to yield an amount (or a content) of the constituent. This amount or content may be termed "apparent". The subsequent data will then confirm the figure in question or show that more than one component is present. If only one component (the suspected one identical to the standard) is present, the "apparent" content will turn out to be invariant with time and the identity is secured by equation (2a) and the following arguments. If the apparent content varies with time, the above-mentioned reasoning for the case of several components is applicable.

EXAMPLE OF AN IDENTIFICATION PROCEDURE: ARE MERCURY AND ARSENIC PRESENT IN THE REMAINS OF THE LATE KING ERIK XIV OF SWEDEN?

Mercury

Samples from the above-mentioned king were obtained in 1958. It has for a long time been a controversial problem in Swedish history whether King Erik XIV was poisoned in 1568 by his brother Johan III

or not. Spectrometric activation analysis was considered to be a possible method of detecting mercury and perhaps arsenic without destroying the samples. They were activated in the D_2O reactor R1* in Stockholm under conditions optimized for the formation of Hg^{197}.

In the case of mercury the mode of activation analysis due to the authors was followed.[3] Gamma spectra were recorded at several instances after an initial aging time (3–4 days). The 77 keV† gamma line was recorded which is easily carried out in a single channel analyser. Below are shown the results of energy comparisons with a standard sample of activated mercury (in the form of a Hg-phenylacetate).

Date 1958	Gamma energy found*	Deviation from standard (%)
February 5	78·5	+ 2·0
February 7	76·5	− 0·7
February 10	75·5	− 2·0
February 11	75·0	− 2·6

* See footnote †

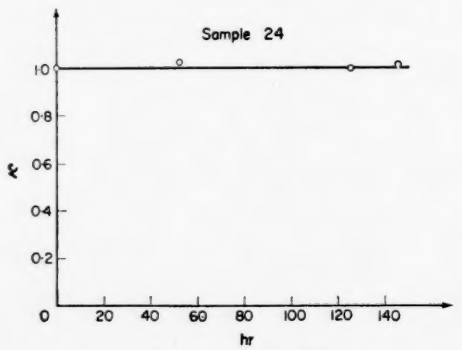

FIG. 1. κ-t-test of suspected Hg^{197} formed in historic remains (see text). It is seen that κ does not deviate from one within the experimental errors and thus the half-life of the activity studied does not deviate from that of the standard. From the data it can be calculated what maximum half-life deviation can be present. The uncertainty of the half-life determination enters the uncertainty rectangle of Fig. 3.

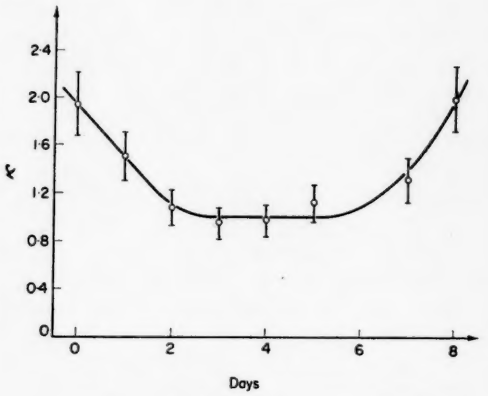

FIG. 2. κ-t-test of As^{76}. It is seen that the activity is not identical with As^{76}. Only for the central part there might be reason for suspecting As^{76}. (See text for further discussions.)

The mean deviation of all determinations was −0·8 keV (−1 per cent).

Fig. 1 shows a "κ-test" on the same sample. It is seen that the experimental points do not deviate systematically from unity during two half-lives. The standard deviation in the half-life was found to be 3 hr.

Now we enlarge the general T–$E\gamma$ chart for neutron reactions in the vicinity of Hg^{197} and introduce the uncertainty of the energy and half-life determinations as is seen in Fig. 2. It is evident that Hg^{197}, and accordingly the presence of mercury, is identified.

From a statistical point of view, it should be attempted to express the uncertainty in the two directions in the same way. In addition, a third axis may be imagined, the probability perpendicular to the T–$E\gamma$-plane. The probability "mountain" thus formed will tell the investigator in a clear manner if there is any chance that a mis-identification is possible. In Fig. 2 one can imagine that the probability "mountain island" hardly interferes with the nearest activity which is Pt^{191}. Moreover, Pt^{191} has eight gamma lines (see below) none of which was seen at all.

In this manner eight different samples

* This belongs to AB Atomenergi.

† The Hg^{197} standard is assumed to be exactly 77·0 keV, even if the peak is known to be constituted by a 68 keV X-ray line and the 77 keV gamma line.

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were non-destructively examined and mercury was found in all of them. The quantitative spectrometric activation analysis was then fulfilled in the usual manner. The result on the poisoning question will be discussed elsewhere.[2]

Arsenic

In other cases the identification may meet with difficulties. Especially the region around 0·5 MeV is difficult because of positron annihilation and a crowding of other lines. The above-mentioned investigation offers such an example, an effort to detect arsenic. An analysis for arsenic was attempted without using chemical dissolutions so that samples could be reserved for future studies. The conditions were optimized for As^{76} and a peak found at about 0·5 MeV was tested. The κ-test* (Fig. 3), normalized to one in the centre, shows systematic deviations. At first sight it may be thought that both short-lived contributions (perhaps Cu^{64}, Na^{24} and K^{42}) and longer lived contribution (probably Br^{82}) are present and that the flat middle part is due to As^{76}. Later, (chemical) determinations (by other workers) showed that this is false. The true arsenic level was actually half the height shown by Fig. 3. Thus it is seen that the κ-test should be used carefully and to identify an activity (κ always equal to one) or the identification should be rejected. With further elaboration it would, however, be possible to resolve say two or perhaps more components from each other. We have not yet attempted such cases.

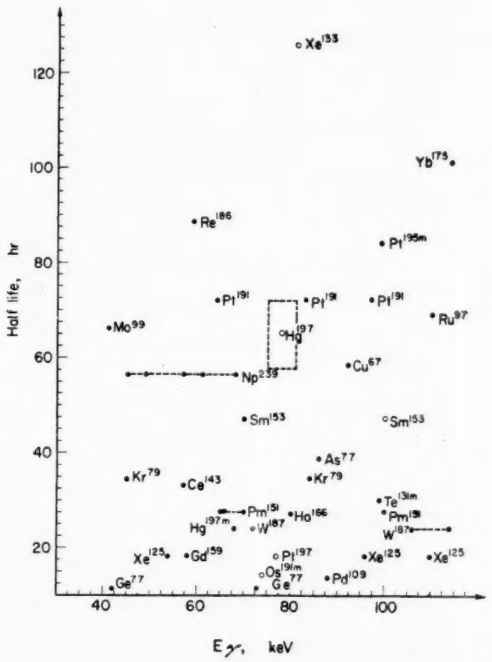

FIG. 3. T-$E\gamma$-chart for the area surrounding Hg^{197}. The uncertainty of half-life (ΔT) and gamma energy ($\Delta E\gamma$) in a certain case (the same as Fig. 1 refers to) forms an uncertainty rectangle around the point for Hg^{197}. It is seen that there are very strong reasons to believe that mercury was present in the sample.

$T - E\gamma$-CHARTS

Because of the usefulness of the $T - E\gamma$-representation we have extended our collection of data on neutron produced nuclides to a large amount of cases encountered in practical work. During the preparation of the charts (Figs. 4 and 5) and their keys (Appendix I and II), it was clear that our selection of nuclides should be presented as clearly as possible. Thus the selection is governed by the following points.

(1) The material presented is based mainly on the STROMINGER–HOLLANDER–SEABORG tables of 1958.[1] E-, F- and G-nuclides of these tables were neglected. We have not found any errors in the tables relevant to our selection. Should errors be present the charts and keys will show these errors.

(2) The charts mainly contain (n, γ)-formed nuclides and active daughter products of these. In addition, (n, p)- and (n, α)-formed nuclides not formed by neutron capture are included in so far as they are experimentally found and the data published. The somewhat strange rule of

* This was due to Mrs. I. Fineman and the senior author.[2]

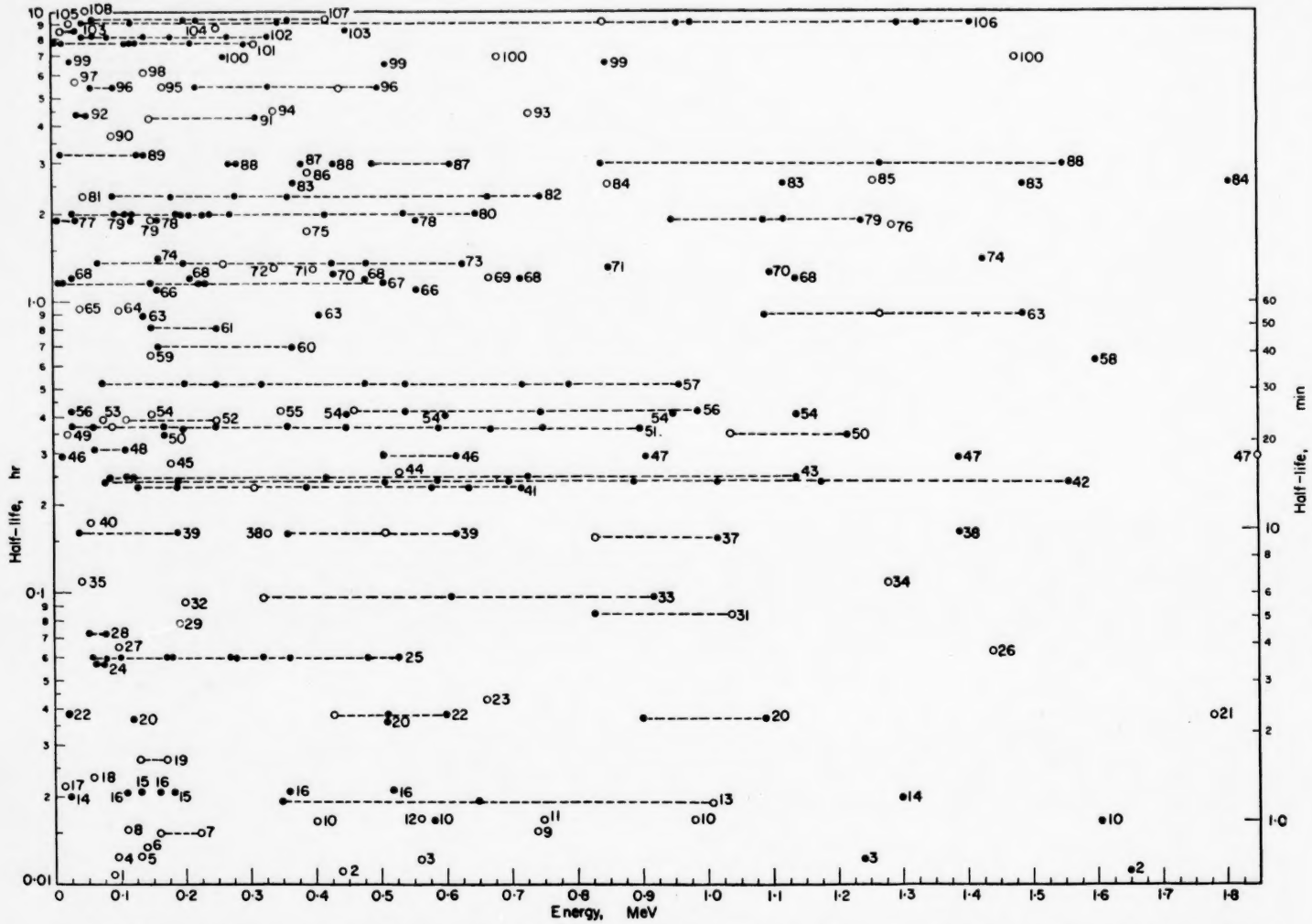

FIG. 4. *T-Eγ*-chart I covering half-lives of 0·01–10 hr. The strongest gamma lines are labelled with open circles. If several gamma lines are emitted from the same nuclide, dots connect the corresponding points. For future reference, if both the half-life and gamma energy of a certain neutron-produced activity have been determined, then locate the corresponding point. Use uncertainty of the two determinations to make the assignment certain. Find the figure of the nuclide and turn to Appendix I for more detailed data for the properties. If several nuclides are possible, try to determine the properties more accurately, or use the intensity data (see Appendix) or perf orm chemical separations. If necessary turn to more complete tables such as STROMIN GER'S[1].

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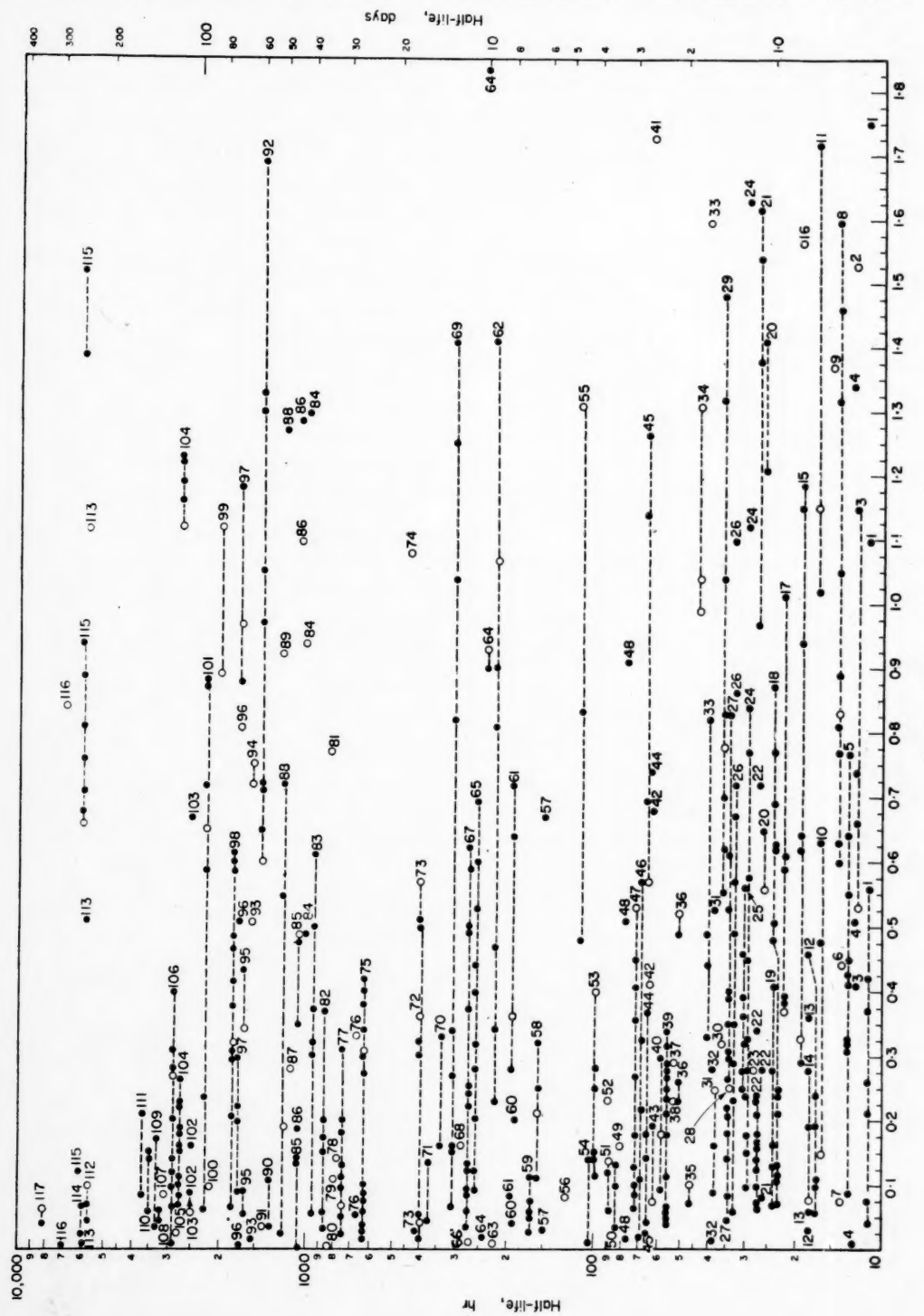

FIG. 5. *T-Eγ*-chart No. II covering 10–10,000 hr. For notes on use, see text of Fig. 4.

selection is: "only those (n, p)- and (n, α)-formed nuclides listed by SAELAND *et al.*[5], MELLISH *et al.*[6], HUGHES[7] and ROCHLIN[8] are included". They should be *A*- or *B*-nuclides according to the STROMINGER tables.

(3) The charts do not include the following:

(a) (γ, n)-formed nuclides.

(b) $(n, 2n)$-formed nuclides.

(c) Nuclides formed by secondary nuclear reactions, e.g. Al^{28} $(t, p)Mg^{28}$ with lithium present.

(d) Nuclides formed by multiple neutron capture.

(e) Natural radioactive or artificially produced elements (either as products or targets), unless they are formed by reactions according to paragraph 2. (There are two exceptions to this rule, namely the formation in Th and U of Th^{233} and Pa^{233}, and U^{239} and Np^{239} respectively.)

(f) Fission products. This is an important restriction of the material. The charts contain 225 nuclides and it is technically very difficult to include the fission products. It seems to be a practical thing to have fission products on separate charts (the authors are ready to prepare such charts if this is of interest). The omission of the fission products should not be so serious practically, because the experimentalist will soon detect, if fissionable matter is present, one or two of the most intense fission nuclides and will then expect the rest of them.

(4) Half-life is restricted to the following regions:

36 sec to 10 hr (0·01–10 hr), chart I and Appendix I

10–10,000 hr chart II and Appendix II.

(5) According to the rules in paragraphs 1–4, only nuclides which possess discrete γ-emission are included. "Pure" beta emitters are thus omitted. However, a special Appendix (III) lists those cases encountered following rules 1–4.

The data are selected according to some extra rules.

Data for gamma transitions are got from the top of the STROMINGER tables, i.e. favouring the most complete and most accurate data. In some cases intensity information was taken from an older work than the one listed first. Only in a few cases are more than three figures given for the gamma energy. In some cases it was necessary to include four in order to distinguish several nearby lines. The reason for these abbreviations is that the data are mainly intended for scintillation spectroscopy of standard kind.

Where more than one gamma line is present, those being less than 1 per cent of the strongest line (wholly neglecting internal conversion considerations and thus also K-X-rays resulting from it) are neglected. If annihilation radiation dominates, this exclusion rule is applied after comparison with the intensity of that radiation.

As is known, certain nuclides emit X-rays after electron capture. This case is termed *EC* in the STROMINGER tables. We have added energy figures for these X-rays. This was made by taking the average of the α_1 and α_2 X-ray emission lines of the element below that showing K-capture. The CAUCHOIS–HULUBEI tables were used throughout.[9] The experimenter should be aware that β-lines and others are present and will modify the apparent energy found.

Where possible the most intense gamma line has been especially labelled in the charts, because this should be a valuable characteristic. In the case of nuclides emitting more than one gamma line, dots have been put between the points.

No data about whether cascade transitions are present or not are included. Data on measured half-life of nuclear states emitting gamma radiation are also excluded as well as all data on internal conversion. The latter point should be noted by less experienced experimenters.

Half-life data are in most cases presented with three figures.

If an activity (which is not listed in the chart despite its half-life and gamma energy being well determined) is found, there may be the following alternatives:

(1) Some error is present in the chart.

(2) It may be a fission product.

(3) It may be a K-X-radiation resulting from internal conversion (0–100 keV).

(4) It may be an activity formed by (γ, n) or $(n, 2n)$-reactions, etc.

(5) A new discovery of unknown nuclear isomer or, less probably, a new nuclide.

It should be emphasized here that strong samples of "pure" beta emitters (see Appendix III) exhibit a continuous "bremsstrahlung" spectrum when a scintillation detector such as NaI(Tl) is used. If heavy elements are also present, the K-X-ray peak may be seen. It should also be remarked that long-lived nuclides are not present if the half-life exceeds about 1 year. There are a few neutron-produced activities which are longer lived and are formed by appreciable cross-section, e.g. Co^{60} and Cs^{134} which are seen in a gamma scintillation detector and spectrometer under suitable intensity circumstances.

In addition to the uses mentioned in the introduction, the tables might be used when it is wished to select a suitable gamma emitter with emission energies in a certain region (e.g. for calibration of spectrometers or detectors, etc.) for some purpose.

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APPENDIX I

Table I corresponds to chart I, i.e. Fig. 4. The Table includes 108 different nuclides found in chart I. The figure to the left is that found in chart I for a certain point. The E_γ table is taken from the STROMINGER–HOLLANDER–SEABORG tables.[1] We use the same intensity terms. Per cent (%) means per cent of the total number of disintegrations. † Refers to relative intensities (without normalization as a rule, although †100 is often used for the strongest line). No data on conversion factors are included. The letter *W* means "weak"; * means (n, p) formed nuclide; ** means (n, α) formed nuclide; *EC* means electron capture.

For further details, see text.

TABLE 1

No.	Nuclide	T	T (hr)	E_γ in MeV and remarks
1	Ag^{109m}	39·2 sec	0·0109	0·088
2	Ne^{23}	40·2 sec	0·0112	0·44(†100)–1·65(†3)
3	Rh^{104}	44 sec	0·0122	0·56(†100)–1·24(†5·8). Daughter of Rh^{104m} (4·4 min)
4	Ag^{107m}	44·3 sec	0·0123	0·093. Daughter of Cd^{107} (6·7 hr)
5	Rh^{105m}	45 sec	0·0125	0·13. Daughter of Ru^{105} (4·5 hr). Decays to Rh^{105} (36·5 hr)
6	Ge^{75m}	48 sec	0·0133	0·14. Decays to Ge^{75} (82 min)

* See also SAELAND's discussion point to Reference 6 in the UNESCO Proceedings. [Table 1 continued overleaf

Table 1 contd.

No.	Nuclide	T	T (hr)	E_γ (MeV) and remarks
7	Ge^{77m}	54 sec	0·0150	0·16(†100)–0·22(†100). Decays partly to Ge^{77} (11·3 hr) and to As^{77} (38·7 hr)
8	Xe^{125m}	55 sec	0·0153	0·11. Decays to Xe^{125} (18·0 hr)
9	Ce^{139}	55 sec	0·0153	0·74. Decays to Ce^{139} (140 days)
10	$^{*}Na^{25}$	60 sec	0·0167	0·40(†10)–0·58(†9)–0·98(†10)–1·61(†3)
11	Nb^{97m}	60 sec	0·0167	0·75. Daughter of Zr^{97} (17·0 hr). Decays to Nb^{97} (72·1 min)
12	Rb^{86m}	61 sec	0·0169	0·56. Decays to Rb^{86} (18·7 days)
13	Se^{83m}	70 sec	0·0194	0·35(†16)–0·65(†20)–1·01(†100)–2·02(†40). Decays to Br^{83} (2·30 hr)
14	In^{114}	72 sec	0·0200	0·0231(*EC*)–1·30 (0·09%). Daughter of In^{114m} (50·0 days)
15	Xe^{127m}	75 sec	0·0208	0·13–0·18. Decays to Xe^{127} (36·4 days)
16	Dy^{165m}	1·25 min	0·0208	0·11–0·16–0·36–0·52. Decays partly to Dy^{165} (2·32 hr)
17	Sb^{124m1}	1·3 min	0·0217	0·012. Decays to Sb^{124} (60·9 days)
18	Ir^{192m}	1·42 min	0·0236	0·058. Decays to Ir^{192} (74·4 days)
19	W^{185m}	1·62 min	0·0270	0·13(†50)–0·17(†50). Decays to W^{185} (75·8 days, no γ)
20	Zn^{71}	2·2 min	0·0367	0·12–0·51–0·90(*W*)–1·09(*W*)
21	Al^{28}	2·27 min	0·0378	1·78 (100%)
22	Ag^{108}	2·3 min	0·0383	0·0211(*EC*)–0·43(†100)–0·51(β^+)–0·60(†79) and others close to 0·60
23	Ba^{137m}	2·6 min	0·0433	0·662
24	Sb^{122m}	3·5 min	0·0583	0·061–0·075. Decays to Sb^{122} (2·80 days)
25	Gd^{161}	3·6 min	0·0600	0·057–0·078–0·10–0·17–0·18–0·27–0·28–0·32–0·36–0·48–0·53. Decays to Tb^{161} (6·88 days)
26	V^{52}	3·76 min	0·0627	1·44 (100%)
27	Se^{79m}	3·91 min	0·0651	0·096
28	Rh^{104m}	4·4 min	0·0733	0·051–0·077. Decays to Rh^{104} (44 sec)
29	Pd^{109m}	4·75 min	0·0791	0·19. Decays to Pd^{109} (13 5 hr)
30	S^{37}	5·04 min	0·0840	3·1 (90%)
31	Cu^{66}	5·1 min	0·0850	0·83(†2·5)–1·04(†100)
32	Hg^{205}	5·5 min	0·0917	0·20
33	Ti^{51}	5·8 min	0·0967	0·32(†96)–0·61(†1·4)–0·92(†4·2)
34	$^{*}Al^{29}$	6·56 min	0·109	1·28 (85%)–2·43 (15%)
35	Nb^{94m}	6·6 min	0·110	0·042
36	Ca^{49}	8·8 min	0·147	3·10(†89)–4·05(†10). Decays to Sc^{49} (57 min–no γ)
37	Mg^{27}	9·45 min	0·157	0·83(†70)–1·02(†30)
38	Sn^{125}	9·5 min	0·158	0·33(99·7%)–1·39 (1·9%)
39	Os^{190m}	9·5 min	0·158	0·039–0·19(†75)–0·36(†90)–0·51(†100)–0·62(†92)
40	Co^{60m}	10·5 min	0·175	0·059 (99 %)
41	Tc^{101}	14·0 min	0·233	0·13(†2·6)–0·19(†2·3)–0·31(†100)–0·39(†1·8)–0·58(†8)–0·64(†1)–0·72 (†1·2). Daughter of Mo^{101} (14·6 min)
42	Mo^{101}	14·6 min	0·243	0·080–0·19–0·51–0·59–0·70–0·89–1·02–1·18–1·56–2·08. Decays to Tc^{101} (14·0 min)
43	Nd^{151}	15 min	0·250	0·085–0·11–0·12–0·42–0·73–1·14. Decays to Pm^{151} (27·5 hr)
44	Xe^{135m}	15·6 min	0·260	0·53. Decays to Xe^{135} (9·13 hr)
45	Ta^{182m}	16·5 min	0·275	0·18. Decays to Ta^{182} (115·1 days)
46	Br^{80}	17·6 min	0·293	0·0112(*EC*)–0·51(β^+)–0·62. Daughter of Br^{80m} (4·38 hr)
47	Rb^{88}	17·8 min	0·296	0·91(†63)–1·39(†6)–1·85(†100)–2·11(†4·5)–2·68(†11)–3·01(†1·4)–3·24 (†1·4)–3·52(†1·1)–4·87(†1·4)
48	Re^{188m}	18·7 min	0·311	0·064–0·11. Decays to Re^{188} (16·7 hr)
49	Sb^{124m2}	21 min	0·350	0·019. Decays to Sb^{124} (60·9 days)
50	Ga^{70}	21·1 min	0·352	0·17(0·44%)–1·04(0·76%)–1·22
51	Th^{233}	22·1 min	0·368	0·029(2·1%)–0·057–0·087(2·7%)–0·17(0·7%)–0·20(0·3%)–0·25–0·36–0·45(1%)–0·59–0·67(0·25%)–0·75–0·90(0·14%). Decays to Pa^{233} (27·0 days)
52	Sm^{155}	23·5 min	0·392	0·11(†100)–0·25(†100). Decays to Eu^{155} (1·7 years)
53	U^{239}	23·5 min	0·392	0·074. Decays to Np^{239} (2·35 days)
54	Te^{131}	24·8 min	0·413	0·15(†100)–0·45(†24)–0·60(†6)–0·95(†4)–1·14(†8) Daughter of Te^{131m} (30·0 hr). Decays to I^{131} (8·08 days)
55	Se^{83}	25 min	0·417	0·35. Decays to Br^{83} (2·30 hr)
56	I^{128}	25 min	0·417	0·0274(*EC*)–0·46(17%)–0·54(1·8%)–0·75(0·3%)–0·99(0·3%)
57	Pt^{199}	31 min	0·517	0·074–0·20–0·25–0·32–0·48–0·54–0·72–0·79–0·96

[Table 1 continued overleaf

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Table 1 contd.

No.	Nuclide	T	T (hr)	E_γ (MeV) and remarks
58	Cl^{38}	37·3 min	0·621	1·60(†100)–2·15(†130)
59	Sn^{123}	39·5 min	0·658	0·15
60	Hg^{199m}	42 min	0·700	0·16–0·37
61	Cd^{111m}	48·6 min	0·810	0·15–0·25
62	Cd^{117}	50 min	0·833	See Cd^{117m} (3·0 hr). The STROMINGER Table does not assign the γ-lines in this case. Decays to In^{117m} (1·90 hr) and In^{117} (1·1 hr)
63	In^{116m}	54·0 min	0·900	0·14(3%)–0·41(25%)–1·09(54%)–1·27(75%)–1·49(21%)–2·09(25%)
64	Se^{81m}	56·8 min	0·947	0·10. Decays to Se^{81} (18·2 min, no γ)
65	Rh^{103m}	57 min	0·950	0·040. Daughter of Pd^{103} (17 days) and Ru^{103} (39·8 days)
66	In^{117}		1·1	0·16–0·56. Daughter of Cd^{117} (50 min) and In^{117m} (1·90 hr)
67	Sr^{85m}	70 min	1·17	0·0075–0·0134(*EC*)–0·15–0·225–0·233–0·51. (Rb^{85m})
68	Te^{129}	72 min	1·20	0·027–0·21–0·48–0·72–1·14. Daughter of Te^{129m} (33·5 days)
69	Nb^{97}	72·1 min	1·20	0·67. Daughter of Nb^{97m} (60 sec)
70	Er^{163}	75 min	1·25	0·43–1·10
71	Kr^{87}	78 min	1·30	0·40(†100)–0·85(†19)–2·05–2·57(†42)
72	Pt^{197m}	78 min	1·30	0·34. Decays to Pt^{197} (18 hr)
73	Ge^{75}	82 min	1·37	0·066(†2·2)–0·20(†12)–0·26(†100)–0·43(†2·5)–0·48(†2·3)–0·63(†1·8). Daughter of Ge^{75m} (48 sec)
74	Ba^{139}	84·0 min	1·40	0·16–1·43
75	In^{113m}	104 min	1·73	0·39. Daughter of Sn^{113} (119 days)
76	A^{41}	110 min	1·83	1·29(99%)
77	Kr^{83m}	114 min	1·90	0·0093–0·033. Daughter of Br^{83} (2·30 hr)
78	In^{117m}		1·90	0·16–0·56. Daughter of Cd^{117} (50 min). Decays to In^{117} (1·1 hr)
79	Yb^{177}		1·90	0·12(†13)–0·15(†100)–0·95(†6)–1·09(†30)–1·12(†4)–1·24(†27)
80	Nd^{149}		2·0	0·030–0·097–0·11–0·12–0·19–0·20–0·21–0·23–0·24–0·27–0·42–0·54–0·65. Decays to Pm^{149} (54 hr)
81	Br^{83}		2·30	0·046. Daughter of Se^{83m} (70 sec) and Se^{83} (25 min). Decays partly to Kr^{83m} (1·90 hr)
82	Dy^{165}		2·32	0·095–0·18–0·28–0·36–0·67–0·75. Daughter of Dy^{165m} (1·25 min)
83	Ni^{65}		2·56	0·37–1·12–1·49
84	Mn^{56}		2·58	0·85(†100)–1·81(†30)–2·13(†20)
85	Si^{31}		2·62	1·26(0·07%)
86	Sr^{87m}		2·80	0·39
87	Zn^{71m}		3·0	0·38–0·49–0·61
88	Cd^{117m}		3·0	0·27–0·28–0·43–0·84–1·27–1·55–2·00 (including lines of Cd^{117}, 50 min)
89	Cs^{134m}		3·2	0·011–0·127–0·137. Decays to Cs^{134} (2·07 years)
90	Lu^{176m}		3·71	0·089
91	Kr^{85m}		4·36	0·15(†57)–0·31(†10). Decays to Kr^{85} (10·3 years)
92	Br^{80m}		4·38	0·037–0·049. Decays to Br^{80} (17·6 min)
93	Ru^{105}		4·5	0·73. Decays to Rh^{105m} (45 sec)
94	In^{115m}		4·5	0·34. Daughter of Cd^{115} (53·0 hr)
95	Pd^{111m}		5·5	0·17. Decays to Pd^{111} (22 min) which in its turn decays to Ag^{111m} (74 sec) and Ag^{111} (7·6 days) not included in the Table
96	Hf^{180m}		5·5	0·058–0·093–0·22–0·33–0·44 (80%)–0·50 (20%)
97	Os^{189m}		5·7	0·031
98	Tc^{99m}		6·04	0·140–0·142. Daughter of Mo^{99} (66·0 hr)
99	Cd^{107}		6·7	0·0221(*EC*)–0·51(β^+)–0·85(0·4%). Decays to Ag^{107m} (44·3 sec)
100	Mo^{93m}		6·95	0·26(†60)–0·68(†100)–1·48(†100)
101	Er^{171}		7·8	0·005–0·012–0·111(†27)–0·116(†3)–0·124(†12)–0·211(†1)–0·296(†42)–0·308(†100). Decays to Tm^{171} (680 days)
102	Dy^{157}		8·2	0·0442(*EC*)–0·061–0·083–0·14–0·18–0·27–0·33
103	Ce^{137}		8·7	0·010(100%)–0·0333(*EC*)–0·45(3%). Daughter of Ce^{137m} (34·5 hr)
104	Xe^{135}		9·13	0·25(†100). Daughter of Xe^{135m} (15·6 min)
105	$^*Co^{58m}$		9·2	0·025. Decays to Co^{58} (71·3 days)
106	Eu^{152}		9·2	0·0399(*EC*, 25%)–0·12–0·34–0·84(†140)–0·96(†100)–0·98–1·30–1·33–1·41
107	Te^{127}		9·4	0·059(0·05%)–0·20–0·22–0·36(0·1%) 0·42(0·8%). Daughter of Te^{127m} (105 days)
108	Er^{165}		10·0	0·0472(*EC*)

APPENDIX II

This appendix refers to of chart II, i.e. nuclides of half-life 10–10,000 hr, for abbreviations and symbols, see text of Appendix I.

TABLE 2

No.	Nuclide	T	T (hr)	E_γ (MeV) and remarks
1	Ge^{77}		11·3	0·042–0·073–0·21–0·26–0·37–0·42–0·56–1·10–1·75. Daughter of Ge^{77m} (54 sec). Decays to As^{77} (38·7 hr)
2	K^{42}		12·5	1·53 (20%)
3	**I^{130}		12·6	0·41(†30)–0·53(†100)–0·66(†90)–0·74(†80)–1·15(†40)
4	Cu^{64}		12·8	0·00748(*EC*)–0·51(β^+)–1·34(0·5%)
5	Pd^{109}		13·5	0·088 (Ag^{109m}, 39·2 sec). 0·307–0·320–0·325–0·412–0·425–0·45–0·55–0·64–0·77. Daughter of Pd^{109m} (4·75 min)
6	Zn^{69m}		13·8	0·44. Decays to Zn^{69} (57 min, no γ)
7	Os^{191m}		14·0	0·074. Decays to Os^{191} (16·0 days)
8	Ga^{72}		14·3	0·60(†7)–0·63(†21)–0·77(†3)–0·81(†3)–0·83(†93)–0·89(†10)–1·05(†7)–1·32(†2)–1·46(†4)–1·60(†6)–1·86(†6)–2·20(†30)–2·49(†10)–2·51(†17)
9	Na^{24}		15·0	1·37(100%)–2·75(100%)
10	Re^{188}		16·7	0·15(†630)–0·48(†67)–0·63(†100). Daughter of Re^{188m} (18·7 min)
11	Zr^{97}		17·0	1·02(†10)–1·15(†20)–1·72(†5). Decays to Nb^{97m}(60 sec)
12	Xe^{125}		18·0	0·0285(*EC*)–0·054–0·096–0·11–0·19–0·24–0·46. Daughter of Xe^{125m} (55 sec). Decays to I^{125} (60·0 days)
13	Gd^{159}		18·0	0·058–0·36
14	Pt^{197}		18·0	0·077(†30)–0·19(†3·9)–0·28(†1). Daughter of Pt^{197m} (78 min)
15	Ir^{194}		19·0	0·29(†5)–0·33(†27)–0·62(†1·7)–0·64(†6)–0·94(†2·9)–1·15(†2·9)–1·18(†1·7), 9 others (*W*)
16	Pr^{142}		19·2	1·57 (4·1%)
17	*K^{43}		22·4	0·37(†100)–0·388(†14)–0·394(†16)–0·59(†23)–0·61(†91)–1·01(†4)
18	W^{187}		24·0	0·072–0·106–0·114–0·13–0·21–0·239–0·246–0·48–0·51–0·619–0·63–0·69–0·77–0·87
19	Hg^{197m}		24·0	0·068(*EC*)–0·13–0·16–0·28–0·41. Decays mostly to Hg^{197} (65 hr)
20	As^{76}		26·4	0·56(†100)–0·65(†9)–1·21(†23)–1·41(†1·5)–2·06(†5)
21	Ho^{166}		27·3	0·080–0·97–1·38–1·54–1·62
22	Pm^{151}		27·5	0·065–0·066–0·070–0·10–0·12–0·14–0·16–0·17–0·18–0·21–0·23–0·24–0·28–0·34–0·72. Daughter of Nd^{151} (15 min)
23	Ba^{135m}		28·7	0·27
24	Te^{131m}		30·0	0·099–0·15–0·18–0·24–0·28–0·33–0·45–0·58–0·77–0·84–1·12–1·63 Decays partly to Te^{131} (24·8 min)
25	Os^{193}		30·6	0·25–0·28–0·32–0·36–0·39–0·46–0·56
26	Ce^{143}		33·0	0·057–0·23–0·29–0·35–0·49–0·57–0·67–0·72–0·86–1·10. Decays to Pr^{143} (13·8 days, no γ)
27	Kr^{79}		34·5	0·045–0·084–0·14–0·18–0·21–0·22–0·26–0·30–0·31–0·35–0·39–0·40––0·53–0·61–0·83
28	Ce^{137m}		34·5	0·25. Decays to Ce^{137} (8·7 hr)
29	Br^{82}		35·9	0·55(†80)–0·62(†50)–0·70(†33)–0·78(†100)–0·83(†30)–1·04(†35)–1·32(†32)–1·48(†21)
30	Rh^{105}		36·5	0·32. Daughter of Rh^{105m} (45 sec)
31	As^{77}		38·7	0·086(0·13%)–0·16(0·26%)–0·25(2·5%)–0·53(0·8%). Daughter of Ge^{77} (11·3 hr)
32	Ba^{133m}		38·8	0·012–0·28. Decays to Ba^{133} (7·2 years)
33	La^{140}		40·2	0·33(†40)–0·44(†6)–0·49(†50)–0·82(†46)–1·60(†100)–2·50(†1)
34	***Sc^{48}		44·0	0·99(†100)–1·04(†100)–1·31(†100)
35	Sm^{153}		47·1	0·070(†7)–0·10(†100)
36	Cd^{115}		53·0	0·23(†10)–0·26(†30)–0·49(†220)–0·52(†430). Decays to In^{115m} (4·5 hr)
37	Pm^{149}		54·0	0·29. Daughter of Nd^{149} (2·0 hr)
38	Xe^{133m}	2·3 days	55·2	0·23
39	Np^{239}	2·35 days	56·5	0·045–0·049–0·057–0·061–0·068–0·11–0·18–0·21–0·23–0·25–0·27–0·28–0·29–0·32–0·34. Decays to Pu^{239} (24360 years)
40	*Cu^{67}		58·5	0·092(†56)–0·18(†100)–0·30(†1·4)
41	Y^{90}		64·2	1·73 (0·02%)

[*Table 2 continued overleaf*

Table 2 contd.

No.	Nuclide	T	T (hr)	E_γ (MeV) and remarks
42	Au^{198}	2·70 days	64·8	0·412(†100)–0·68(†1·1)
43	Hg^{197}		65·0	0·078(99 %)–0·19(1·2%). Daughter of Hg^{197m} (24·0 hr)
44	Mo^{99}		66·0	0·041–0·14–0·18–0·37–0·74. Decays to Tc^{99m} (6·04 hr)
45	Sb^{122}	2·80 days	67·2	0·0252(*EC*)–0·57(66%)–0·69(3·4%)–1·14(0·7%)–1·26(0·7%). Daughter of Sb^{122m} (3·5 min)
46	Ru^{97}	2·88 days	69·1	0·0184(*EC*)–0·11–0·22–0·33–0·57. Decays to Tc^{97m} (91 days)
47	Pt^{191}	3·00 days	72·0	0·0642(*EC*)–0·083–0·097–0·13 (†50)–0·18(†40)–0·27(†20)–0·36(†100)–0·41(†80)–0·45(†20)–0·53(†170)
48	$^{**}Zr^{89}$		79·3	0·0149(*EC*)–0·51(β^+)–0·91(Y^{89m})
49	$^{*}Sc^{47}$	3·43 days	82·4	0·16(60%). Daughter of Ca^{47} (4·7 days)
50	Pt^{195m}	3·5 days	84·0	0·031–0·099–0·13
51	Re^{186}		88·9	0·0588(*EC*)–0·123(2%)–0·137 (22%)
52	Nb^{95m}		90·0	0·23. Daughter of Zr^{95} (65 days)
53	Yb^{175}		101	0·114(†31)–0·138(†2·2)–0·145(†5·9)–0·25(†3·8)–0·28(†62)–0·40(†100)
54	Pt^{193m}	4·3 days	103	0·013–0·14
55	Ca^{47}	4·7 days	113	1·31(†65)–0·83(†5)–0·48(†5). Decays to Sc^{47} (3·43 days)
56	Xe^{133}	5·27 days	126	0·081(100%)
57	$^{*}Cs^{132}$	6·2 days	149	0·0296(*EC*)–0·67
58	Lu^{177}	6·75 days	162	0·11(†100)–0·21(†220)–0·25(†3)–0·32(†3)
59	Tb^{161}	6·88 days	165	0·026–0·027–0·049–0·057–0·075–0·078–0·11. Daughter of Gd^{161} (3·6 min)
60	Xe^{129m}	8·0 days	192	0·040–0·20
61	I^{131}	8·08 days	194	0·082(2·2%)–0·28(5·3%)–0·36(80%)–0·64(9%)–0·72(3%). Daughter of Te^{131} (24·8 min). Decays partly to Xe^{131m} (12·0 days)
62	Sn^{125}	9·4 days	226	0·23–0·34(†9)–0·47(†16)–0·81(†50)–0·90(†30)–1·07(†100)–1·41(†6)–1·96–(†24). Decays to Sb^{125} (2·0 years)
63	Er^{169}	9·4 days	226	0·008
64	$^{*}Nb^{92}$	10·1 days	242	0·0158(*EC*)–0·90(†1)–0·93(†98)–1·83(†2)
65	Nd^{147}	11·1 days	268	0·091–0·12–0·20–0·28–0·32–0·40–0·44–0·53–0·60–0·69. Decays to Pm^{147} (2·64 years)
66	Ge^{71}	11·4 days	274	0·00926(*EC*)
67	Ba^{131}	11·5 days	276	0·0309(*EC*)–0·055–0·079–0·092–0·12–0·13–0·22–0·24–0·25–0·37–0·49–0·50–0·59–0·62. Decays to Cs^{131} (9·6 days—no γ)
68	Xe^{131m}	12·0 days	288	0·16
69	$^{*}Cs^{136}$	12·9 days	310	0·067–0·15–0·16–0·27–0·34–0·82–1·04–1·25–1·41–2·35–2·49
70	Sn^{117m}	14 days	336	0·16–0·33
71	Os^{191}	16·0 days	384	0·042–0·13. Daughter of Os^{191m} (14·0 hr)
72	Pd^{103}	17 days	408	0·0202(*EC*)–0·040(†2·1)–0·053–0·30(†0·3)–0·32(†0·1)–0·36(†2·1)–0·50(†0·5). Decays to Rh^{103m} (57 min)
73	Te^{121}	17 days	408	0·0263(*EC*)–0·51(13%)–0·57(87%). Daughter of Te^{121m} (154 days)
74	Rb^{86}	18·7 days	448	1·08(8·9%). Daughter of Rb^{86m} (61 sec)
75	Pa^{233}	27·0 days	648	0·016–0·028–0·040–0·058–0·075–0·086–0·10–0·27–0·30(†22)–0·31(†150)–0·34(†6)–0·38–0·40–0·42. Daughter of Th^{233} (22·1 min). Decays to U^{233} ($1{\cdot}62 \times 10^5$ years)
76	Cr^{51}	27·8 days	667	0·0496(*EC*)–0·33(9%)
77	Yb^{169}	31·8 days	764	0·0503(*EC*)–0·023(†20)–0·064(†25)–0·094(†3·4)–0·11(†14)–0·13(†9)–0·18(†15)–0·20(†21)–0·31(†6)
78	Ce^{141}	33·1 days	795	0·14
79	Te^{129m}	33·5 days	805	0·11. Decays to Te^{129} (72 min)
80	A^{37}	35·0 days	840	0·0026(*EC*)
81	$^{*}Nb^{95}$	35 days	840	0·77. Daughter of Zr^{95} (65 days)
82	Xe^{127}	36·4 days	874	0·0285(*EC*)–0·057–0·15–0·17–0·20–0·37. Daughter of Xe^{127m} (75 sec)
83	Ru^{103}	39·8 days	956	0·055–0·30–0·32–0·37–0·50–0·61. Decays to Rh^{103m} (57 min)
84	Cd^{115m}	43 days	1030	0·49(†10)–0·94(†74)–1·30(†31)
85	Hf^{181}	44·6 days	1070	0·0039–0·133(†7)–0·136(†1)–0·137(†0·3)–0·35(†2·3)–0·476(†0·3)–0·482(†14)

[*Table 2 continued overleaf*

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Table 2 contd.

No.	Nuclide	T	T (hr)	E_γ (MeV) and remarks
86	Fe^{59}	45·1 days	1080	0·19(2·8%)–1·10(57%)–1·29(43%)
87	Hg^{203}	46·9 days	1130	0·28
88	In^{114m}	50·0 days	1200	0·0231(*EC*)–0·19(†100)–0·55(†19)–0·72(†19)–1·27(†1·2). Decays to In^{114} (72 sec)
89	Sr^{89}	50·5 days	1220	0·92(0·01%)
90	Te^{125m}	58 days	1390	0·036–0·11
91	I^{125}	60·0 days	1440	0·035. Daughter of Xe^{125} (18·0 hr)
92	Sb^{124}	60·9 days	1460	0·60(†100)–0·65(†6)–0·71(†4)–0·72(†11)–0·97(†5)–1·05(†2)–1·30(†1·3)–1·33(†2)–1·69(†52)–2·09(†7). Daughter of Sb^{124m1} (1·3 min) and Sb^{124m2} (21 min)
93	Sr^{85}	64 days	1540	0·0134(*EC*)–0·51(100%)
94	Zr^{95}	65 days	1560	0·72(49%)–0·75(49%). Decays to Nb^{95m} (90 hr) and Nb^{95} (35 days)
95	Hf^{175}	70 days	1680	0·0536(*EC*)–0·089(†40)–0·343(†1000)–0·433(†16)
96	*Co^{58}	71·3 days	1710	0·0064(*EC*)–0·51(β^+ — †30)–0·81(†100). Daughter of Co^{58m} (9·2 hr)
97	Tb^{160}	72·3 days	1740	0·087(†100)–0·20(†30)–0·22(†25)–0·30(†200)–0·88(†220)–0·97(†260)–1·18(†110)
98	Ir^{192}	74·4 days	1790	0·0624(*EC*)–0·206(†39)–0·296(†360)–0·309(†350)–0·317(†1000)–0·375(†19)–0·417(†16)–0·468(†640)–0·485(†39)–0·588(†71)–0·605(†140)–0·613(†84). Daughter of Ir^{192m} (1·42 min)
99	Sc^{46}	83·9 days	2020	0·89(100%)–1·12(100%)
100	Tc^{97m}	91 days	2180	0·097. Daughter of Ru^{97} (2·88 days). Decays to Tc^{97} ($2{\cdot}6 \times 10^6$ years)
101	Os^{185}	93·6 days	2250	0·0605(*EC*)–0·233(†1·5)–0·59(†1·3)–0·65(†100)–0·72(†5·1)–0·87(†9)–0·88(†9)
102	Te^{123m}	104 days	2500	0·089–0·16
103	Te^{127m}	105 days	2520	0·059(†66)–0·089(†13)–0·67(†1·7). Decays to Te^{127} (9·4 hr)
104	Ta^{182}	115·1 days	2760	0·066(†8)–0·067(†85)–0·085(†5)–0·100(†40)–0·114(†8)–0·116(†1·7)–0·152(†35)–0·156(†12)–0·179(†16)–0·19(†8)–0·222(†35)–0·229(†20)–0·264(†22)–1·12(†100)–1·16(†7)–1·19(†45)–1·22(†95)–1·23(†50). Daughter of Ta^{182m} (16·5 min)
105	Sn^{113}	119 days	2860	0·0242(*EC*). Decays to In^{113m} (104 min)
106	Se^{75}	121 days	2910	0·0105(*EC*)–0·066(†2)–0·097(†7)–0·12(†28)–0·14(†94)–0·20(†3)–0·27(†100)–0·28(†46)–0·31(†2)–0·40(†25)
107	Tm^{170}	129 days	3100	0·084(24%)
108	Dy^{159}	134 days	3220	0·0442(*EC*)–0·058
109	Ce^{139}	140 days	3360	0·0333(*EC*)–0·17. Daughter of Ce^{139m} (55 sec)
110	W^{181}	145 days	3480	0·057(*EC*)–0·14(*W*)–0·15(*W*)
111	Te^{121m}	154 days	3700	0·082–0·21. Decays to Te^{121} (17 days)
112	Gd^{153}	236 days	5670	0·0413(*EC*)–0·069(†20)–0·098(†100)–0·10(†100)
113	Zn^{65}	245 days	5880	0·0081(*EC*)–0·51(β^+)–1·12(44%)
114	Sn^{119m}	250 days	6000	0·024–0·065
115	Ag^{110m}	253 days	6070	0·12–0·66(†100)–0·68(†12)–0·71(†18)–0·76(†24)–0·81(†6)–0·89(†75)–0·94(†25)–1·39(†20)–1·52(†13)
116	*Mn^{54}	291 days	6980	0·0054(*EC*)–0·84(100%)
117	Sm^{145}	340 days	8160	0·0385(*EC*)–0·061(92%). Decays to Pm^{145} (18 years)

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APPENDIX III

Table of "pure" beta emitters. "Pure" means that no γ-lines are listed in the STROMINGER–HOLLANDER–SEABORG tables. Thus Sr^{89}, which has a 0·02 % γ-line, is not listed here but is present in chart II, etc. The nuclides are ordered in half-lives. The latter are never lower than 0·01 hr (36 sec) or longer than 10,000 hr, i.e. the same limits as in the gamma charts.

TABLE 3

Nuclide	Half-life	Maximum β-energy
Cr^{55}	3·52 min	2·85
Xe^{137}	3·9 min	3·5
Tl^{206}	4·19 min	1·51
Se^{81}	18·2 min	1·38
Sc^{49}	57 min	2·05
Zn^{69}	57 min	0·90
Pb^{209}	3·30 hr	0·64
Sn^{121}	27·5 hr	0·38
Bi^{210}	5·01 days	1·16
P^{32}	14·2 days	1·71
P^{33}	25·3 $\pm$ 0·5* days	0·25
S^{35}	87 days	0·17
Sn^{123}	136 days	1·42
Ca^{45}	164 days	0·25
Tl^{204}	3·56 years	0·76

* This is a new determination made in this laboratory. The results will be published elsewhere.

APPENDIX IV

Gamma lines above 1·85 MeV. (These lines are listed here because the charts do not cover this region).

Amendment to Table 1 (half-lives 0·01–10 hr)

No.	Nuclide	Half-life	E_γ (MeV)
13	Se^{83m}	70 sec	2·02
30	S^{37}	5·04 min	3·1
34	*Al^{29}	6·56 min	2·43
36	Ca^{49}	8·8 min	3·10–4·05
42	Mo^{101}	14·6 min	2·08
47	Rb^{88}	17·8 min	2·11–2·68–3·01–3·24–3·52–4·87
58	Cl^{38}	37·3 min	2·15
63	In^{116m}	54·0 min	2·09
71	Kr^{87}	78 min	2·05–2·57
84	Mn^{56}	2·58 hr	2·13
88	Cd^{117m}	3·0 hr	2·00

Amendment to Table 2 (half-lives 10–10,000 hr).

No.	Nuclide	Half-life	E_γ (MeV)
8	Ga^{72}	14·3 hr	1·86–2·20–2·49–2·51
9	Na^{24}	15·0 hr	2·75
20	As^{76}	26·4 hr	2·06
33	La^{140}	40·2 hr	2·50
62	Sn^{125}	9·4 days	1·96
69	*Cs^{136}	12·9 days	2·35–2·49
92	Sb^{124}	60·9 days	2·09

* Formed by (n, p)-reaction.

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Activation Analysis of Cadmium in Small Biopsy Samples

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Biopsy samples of human kidney, comprising only 2–15 mg, were successfully analysed for cadmium by activation analysis. The procedure adopted was, after reactor irradiation and dissolution, a sulphide precipitation which is treated by alkali. For accurate work a final phosphate precipitation is used but in many cases the first precipitate is studied directly by means of a gamma-scintillation spectrometer and multichannel analyser.

LE DOSAGE PAR ACTIVATION DU CADMIUM DANS DE PETITS ÉCHANTILLONS PRIS PAR LA BIOPSIE

On a réussi à faire le dosage par activation du cadmium dans des échantillons de biopsie du rein humain qui étaient de 2–15 mg. seulement. On adopta comme procédé le rayonnement dans le réacteur et la dissolution suivis d'une précipitation de sulfure qui fut alors traité d'alcali. Pour du travail exacte on emploie finalement une précipitation de phosphate mais en bien des cas le premier précipité est soumis directement à un spectromètre à scintillement gamma et à un analysateur à cannelation multiplexe.

АКТИВАЦИОННЫЙ АНАЛИЗ НА КАДМИЙ В НЕБОЛЬШИХ ПРОБАХ, ВЗЯТЫХ ДЛЯ БИОПСИИ

Содержание кадмия в пробах почечных тканей человека, взятых для биопсии (от 2 до 15 мг), было определено активационным анализом. Методика определения состояла в том, что после облучения в реакторе и растворения осажденный сульфид обрабатывался щелочью. Для более точного анализа применялся переосажденный осадок сульфата, но во многих случаях первый полученный осадок исследовался непосредственно помощью гамма-сцинтиляционного спектрометра и многоканального анализатора.

AKTIVIERUNGS-ANALYSE VON CADMIUM IN KLEINEN BIOPSIPROBEN

Biopsiproben menschlicher Niere von 2–15 mg wurden mit Erfolg mit Hilfe der Aktivierungs-Analyse auf ihren Cd-Gehalt untersucht. Das verwendete Verfahren war, nach Reaktor-Bestrahlung und Lösung, eine Sulfidfällung, welche mit Alkali behandelt wird.

Für genauere Untersuchungen wird abschliessend eine Phosphatfällung durchgeführt, jedoch wurde in vielen Fällen schon die erste Fällung direkt mit Hilfe eines γ-Szintillations-spektrometers mit Vielkanalanalysator untersucht.

INTRODUCTION

In connexion with some cadmium poisoning cases, the problem was raised by Dr. B. Axelsson, The National Institute of Public Health, of Stockholm, whether activation analysis was sensitive enough to detect quantitatively the presence of cadmium in rather small kidney samples taken by the physician by means of a special needle technique during local anaesthesia on living people. These samples weigh only 2–14 mg. Somewhat larger samples are available from surgical operations, e.g. from kidney, liver and gall bladder (100–500 mg). Also here, the cadmium activation analysis method was of interest but, of course, the analysis can be made with other methods as well. Cadmium

analysis is of interest also in the case of food.[13]

Cadmium constitutes a favourable case for activation analysis. The method has been used by BROOKSBANK *et al.*[1] and by LEDDICOTTE *et al.*,[2] KANT *et al.*[3] and THOMSON *et al.*[4]. In these cases, chemical separation and beta (or gamma) counting was used. We shall here deal mainly with a combined chemical separation and gamma spectrometrical variant of the method.

NUCLEAR-PHYSICAL DATA AND ACTIVATION PROCEDURES

Natural cadmium has several stable isotopes. Activation by means of neutrons yields activities with half-lives ranging from 3 hr (Cd^{117m}) to 5·1 years (Cd^{113m}). Most of the previous activation analytical work on cadmium has employed Cd^{115} (53 hr) and only occasionally Cd^{115m}.[1,2] The elemental cross-section for thermal neutrons is no less than 2450 barns and, for activation to Cd^{115}, 0·32 barns.[11]

In this laboratory, extensive experience had been collected on the activation analysis of mercury, using Hg^{197} with 65 hr half-life, for a variety of materials including biological ones[8]. This half-life enables the most usual activities induced in biological materials to be aged down, namely Cl^{38} (37 min), Mn^{56} (2·6 hr), Na^{24} (15·0 hr), Cu^{64} (12·7 hr), K^{42} (13 hr) and Zn^{69m} (13 hr). As stated above, in cadmium, Cd^{115} with a half-life of 53 hr is formed among other active Cd isotopes. This half-life is of a similar magnitude to that of Hg^{197}. The use of Cd^{115} was therefore chosen for the activation analysis in the hope that it might be detected by direct scintillation spectrometric analysis without chemical separation. Should this prove to be impossible, the use of Cd^{115} would still allow the aging of the most important activities so that chemical procedures might be performed far from the reactor site and with moderate radiation shielding.

No other cadmium activity will interfere in practice with Cd^{115} if an activation time of 2–3 days and an aging time of, say, 2 days are used. The formation of the longer-lived isomer Cd^{115m} (43 days) has also to be considered. It is formed with a thermal neutron cross-section of 0·04 barns[11] as compared with 0·32 barns for Cd^{115}. Provided the activation time is equal to the half-life for Cd^{115} (53 hr), the activity ratio is about one hundred and then decreases with time. Cadmium-115*m* emits 0·49 MeV (0·3 per cent) and 0·94 MeV (2·3 per cent) and 1·30 MeV (1 per cent) gamma lines.[11] Cadmium-115 emits[11] 0·49 MeV (12 per cent) and 0·52 MeV (25 per cent) and, via the daughter In^{115m} (4·5 hr half-life), 0·34 MeV (47 per cent referred to the number of Cd^{115} disintegrations in equilibrium). If we consider the contamination situation which is probably worst, viz. that of the 0·49 MeV line, the contribution from Cd^{115} should be several hundred times that of Cd^{115m}. The 0·34 MeV line from Cd^{115m} does not seem to decay to Cd^{115} according to the latest isotope tables.[10] Thus, under these conditions, we may disregard Cd^{115m} completely since scintillation spectrometry is not able to detect its contribution in this case.

The daughter product of Cd^{115}, namely In^{115m}, is important since chemical procedures might change the equilibrium between these two. Thus, the measuring samples should be aged for several times the half-life, 4·5 hr, of In^{115m} before spectrometry is done on the 0·34 MeV line. The use of the 0·5 MeV line (superposition of the 0·49 MeV and 0·52 MeV lines) is satisfactory from this point of view. However, this very region may cause trouble because a number of activities formed in neutron-activated tissue appear here, e.g. Cu^{64}, Zn^{65}, As^{76}, Br^{82}, Au^{198}, and annihilating radiation produced indirectly by high energy gammas. If a very careful chemical separation is made, these activities can be ruled out. On the other hand, the total procedure might be less time-consuming if we make a group separation of cadmium followed by scintillation spectrometry. The spectra will show directly if disturbances are present and permit a quantitative assay by means of comparisons

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with standards. The results described will show that this mode of operation is successful. (Despite the very high cross-section of the element cadmium, the flux depression is still less than 1 per cent.) Concerning other errors due to differences in activation flux, a more detailed discussion is given in the paper on the activation analysis of mercury.[8] In the case of cadmium considered here, the errors are of the same magnitude, i.e. only a few per cent.

SPECTROMETRIC ANALYSIS

Some attempts have been made to detect cadmium directly in the activated biological samples by means of gamma scintillation spectrometry. To this end, aging after irradiation is essential.

Gamma scintillation spectra were recorded 6–9 days after irradiation with a NaI(Tl) detector and a single channel analyser. The apparent cadmium content in certain samples, as found by a small but discernible peak, was evaluated by means of known standards. The figures obtained (about 20 μg in a 100 mg liver sample) were reasonably constant during this decay time, indicating that no considerable interference due to activities of other half-lifes can be present in the peak studied. This method of identification and proving that the activity is pure will be published separately.[9] Pieces of different parts of bladder were also investigated, but here only upper limits for the cadmium content could be given ($<$6–10 p.p.m.). Although successful in the case of liver samples of high Cd contamination level, the spectrometric method was not found satisfactory in general, since it requires the repeated recording of spectra in order to ensure that the gamma peak found is due to Cd^{115}–In^{115m}. In the next section, we will therefore turn to a description of separations used prior to spectrometry.

DISCUSSION OF CHEMICAL PROCEDURES

Since the direct spectrometric analysis described above has severe limitations, a chemical separation was considered. It was found that a group separation of the cadmium after addition of a carrier during dissolution solved the problem. This general idea of combining, in activation analysis, group separation and gamma spectrometry was apparently first used by BLANCHARD *et al.*[12] This combination should, according to our experience also from other investigations than the present, be stressed strongly for a lot of cases in activation analysis since it minimizes labour without sacrificing identification and precision. The classical path ending with β-counting (GM-tubes or proportional counters) has to provide a carefully purified final sample. This path is still the only alternative when low activities are induced[3,4] but, for a lot of cases, the sensitivity by use of a NaI scintillation detector and gamma spectrometer together with a multichannel analyser is still sufficient. This was found to be true in the present case.

The procedure followed was the classical sulphide precipitation in acid solution[1,3,4] although there are recent proposals of more refined methods.[5,6] A treatment of the precipitate with sodium hydroxide not only removes excess alkali and halogen ions but also dissolves the Mo, Sn, Pt, Au, As and Sb sulphides.[4]

The procedure is very simple. It does not lead to a completely pure Cd-activity as is seen from gamma spectra (cf. below). The contaminants are probably partly Cu^{64} but this was not investigated in any detail because the 340 keV Cd^{115}–In^{115m} peak is not contaminated and could be easily evaluated without difficulties in our case. Should it be desirable in other cases to purify further, then the method described by THOMSON[4] and others involving $CdNH_4PO_4$ precipitation should be followed.

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CHEMICAL AND GAMMA-SPECTROMETRIC PROCEDURE ADOPTED

Irradiation of samples and standards

Samples of known weight are put into quartz ampoules and sealed.[8] (Dry samples can be put into polythene flasks.) Two forms of standards are prepared, one comprising 0·1 ml $CdSO_4$ solution of known concentration placed in a sealed quartz ampoule (standard I) and the second being a pure piece of filter paper, on which a known $CdSO_4$ solution has been dropped and dried, placed in a polythene flask (standard II). (The standard is in both cases in the interval 5–10 γ Cd.) An irradiation may contain five samples and two or three standards. The samples are irradiated for 2–3 days at about 10^{12} n/cm^2 sec (thermal).

Chemical procedure

After irradiation, the samples are aged for a few hours or overnight. Then, each ampoule is cut into halves and put into a beaker together with 1 ml $CdSO_4$ solution (containing ~10 mg Cd as carrier) and 5 ml fuming HNO_3. The mixture is heated on a water bath until the solution becomes completely clear (a few minutes for a small sample and not much more for a larger one). The solution is transferred to an Erlenmeyer flask (150 ml) and the ampoule pieces are rinsed repeatedly. After diluting to 120 ml (the resulting acid concentration should be 1 Molar), CdS is precipitated by bubbling with H_2S for 5 min. After some hours, the liquid is filtered through a fine pore porcelain filter, then the filter is rinsed with a few ml 1 N NaOH and then with distilled water.

Standard I is treated in the same manner. If the second standard only is used, i.e. when a higher accuracy is required, then it is best to determine the dissolved CdS precipitate either by polarography[7] or by a standard $CdNH_4PO_4$ precipitation[1,3,4] or some other method.

Gamma spectrometry

The gamma spectrum in the region 100–600 keV was registered with a 3 × 3 in. NaI-crystal* and a multichannel analyser. (A single-channel analyser can be used when higher activities are present.) The registration was repeated some days later to obtain a half-life determination.

Curves were drawn and a reasonable background subtraction of the 340 keV line was made. The peak area was compared with that of the standard II, and the amount of Cd was calculated.

Corrections were made for carrier losses either by the figure obtained for the Cd-carrier recovered or, if considerable experience was available on the constancy of these losses, by comparing standards I and II.

RESULTS

From about thirty successful cadmium determinations of the kind described, we can summarize our experience (using the chemical procedure described) in the following manner.

(1) Cadmium is easily detected using the chemical procedure described and multichannel gamma spectrometry of the 340 keV peak. Typical quantities determined were 0·5–3 μg in 2–10 mg samples from kidney biopsies (Cd-exposed workmen). The results are summarized in Table 1.

(2) The lower limit at a flux of 10^{12} n/cm^2 sec may be inferred to be about 0·1 μg although only some experience is available near this limit (cf. Table 1). LEDDICOTTE states a limit of 0·01 μg in his Geneva paper.[2] However, THOMSON *et al.*[4] and KANT *et al.*[3] observed as little as 0·0002 p.p.m. in some semi-conductor materials but, in this case, full purification and beta counting was used.

(3) The large samples (150–300 mg obtained from surgical operations and

* This crystal size has been used by us, but it is obvious that a smaller one would be equally useful.

TABLE 1. Cadmium determinations on small kidney samples taken by biopsy from exposed workmen

Sample No.	Sample weight (mg)	Cd (μg)	Cd (p.p.m.)
1	14	2·3	180
2	3	0·6	200
3	2·7	0·87	320
4	10·3	1·58	150
5	4·0	1·27	320
6	4·9	1·61	330
7	3·1	0·59	190
8	4·7	0·10	21
9	5·9	2·63	446
10	2·9	0·15	52
11	8·0	$\leqq$0·21	$\leqq$26

originating from different parts of the kidney, gall-bladder and liver) provided no difficulties. Contents ranging from 40–300 p.p.m. Cd have been observed. In one case, no Cd was observed and, from that particular determination, a lower limit of 0·4 μg could be set.

The large samples could certainly have been analysed with other methods, e.g. polarography. In a few of these samples, the Cd content was determined both by activation analysis and by polarography (the latter by Dr. Axelsson), and the two values agreed satisfactorily.

The method is illustrated by means of two Figures. Fig. 1 shows a standard spectrum of Cd^{115}. The 340 keV peak is well resolved and has the correct half-width. The 0·5 MeV peak may be somewhat contaminated by annihilation radiation and contributions from Cd^{115} and by a longer-lived, unidentified nuclide.

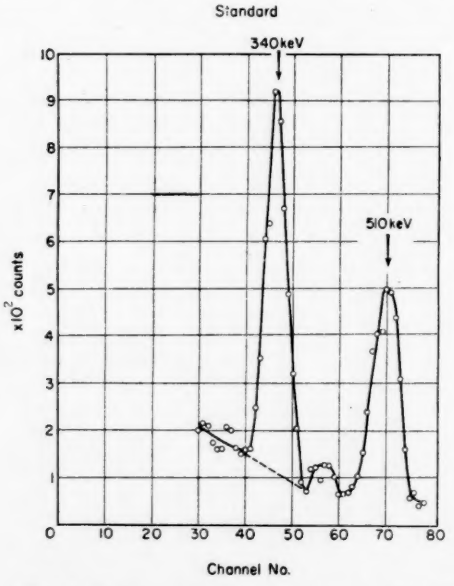

FIG. 1. Gamma scintillation spectrum of a Cd-standard. The activity is due to Cd^{115} (53 hr). The peak at 340 keV is the typical one. (It is actually due to the daughter product In^{115m}.) The 510 keV peak may often be contaminated with impurities.

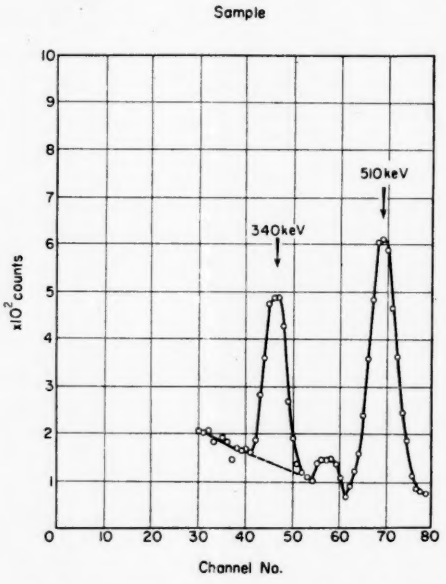

FIG. 2. Gamma scintillation spectrum of a small activated sample of kidney (14 mg). The quantitative analysis is made using the 340 keV peak.

Fig. 2 shows a spectrum of Cd^{115} obtained from a 14 mg kidney sample treated using the procedure described. The 340 keV peak was followed with time and the half-life was determined from semi-log plots. The half-life found for the standards and samples agreed with the literature figure (53 hr) to within the experimental accuracy.

The analytical results are of considerable interest in connexion with the toxicology of cadmium. They indicate how the cadmium content is related to the symptoms of the

patients and how it is distributed within the kidney and other organs of exposed persons. These results will be reported in a special publication by Dr. B. Axelsson.

It should be added that, judging from a recent discussion by VON STURM[7], polarography should be applicable even on the small samples. The sensitivity limit is according to this author[7] (Tabelle 2, p.14) 0·001 μg for cadmium, when using small volumes and square-wave polarography. For direct-current polarography the limit is about 0·01 μg. Whether these possibilities can be realized or not (considering disturbing elements), is not known for these kidney samples.

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Olefin Polymerization in Solutions of $TiCl_4$ in *N*-Heptane Irradiated with Gamma Rays or Electrons

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It is shown that the polymerization of ethylene by radiation-induced catalyst formation in $TiCl_4$–heptane mixture is possible but energetically inefficient. The yield is increased by increasing the $TiCl_4$/heptane ratio but at high ratios chlorination of the polymer can be expected. Lower temperatures favour polymer formation.

Polymerization of propylene by the same process gives relatively large amounts of oily products and very little solid polypropylene.

LA POLYMÉRIZATION DES OLÉFINES DANS DES SOLUTIONS DU $TiCl_4$ DANS LA *N*-HEPTANE IRRADIÉES DE RAYONS GAMMA OU D'ÉLECTRONS

On démontre que la polymérization de l'éthylène par la formation d'un catalyseur induite par le rayonnement dans le mélange $TiCl_4$-heptane est possible mais inefficace du point de vue d'énergie. Le rendement augmente avec augmentation du rapport $TiCl_4$ heptane, mais en les cas de grande rapports il faut s'attendre à la chlorination de la polymère. Les températures moins élevées favorisent la formation de la polymère.

La polymérization du propylène par le même procédé donne des quantités rélativement fortes de produits huileux et très peu de polypropyléne solide.

ПОЛИМЕРИЗАЦИЯ ОЛЕФИНА В РАСТВОРАХ $TiCl_4$ С Н-ГЕПТАНОМ ПОД ДЕЙСТВИЕМ ГАММА-ЛУЧЕЙ ИЛИ ЭЛЕКТРОНОВ

Показано, что полимеризация этилена, вызванная катализатором, образующимся в облучаемой смеси $TiCl_4$ с гептаном, возможна, но энергетически неэффективна. Вывод можно увеличить, повышая отношение $TiCl_4$/гептан, но при высоких значениях можно опасаться хлорирования полимера.

Такая же полимеризация этилена дает сравнительно большие количества маслянистых продуктов и очень малое количество твердого полипропилена.

OLEFINPOLYMERISATION IN LÖSUNGEN VON $TiCl_4$ IN *N*-HEPTAN MIT γ-ODER ELEKTRONEN-BESTRAHLUNG

Es wird gezeigt, dass die Polymerisation von Äthylen durch strahlungsinduzierte Karalysatorbildung in $TiCl_4$-Heptan Gemischen zwar möglich, aber energetisch ungünstig ist. Die Ausbeute zeigt mit zunehmendem $TiCl_4$/Heptan Verhältnis, doch kann bei hohen Verhältniswerten Chlorierung des Polymers erwartet werden. Niedere Temperaturen begünstigen die Polymer-Bildung. Polymerisation von Propylen durch den gleichen Prozess gibt relativ grosse Mengen öliger Produkte und sehr wenig festes Polypropylen.

INTRODUCTION

As a result of the discovery by ZIEGLER[1] of a process for the polymerization of olefins under very mild pressure and temperature conditions, the search for an ethylene polymerization technique using ionizing radiations, based on the idea of lowering by means of radiation the high pressures and temperatures involved in the I.C.I. process,

became uneconomic, and work on the subject rapidly declined.

However, interest in the use of radiation in polymerization processes continued, and perhaps because of certain difficulties encountered, at least temporarily, with the Ziegler process, namely the explosive nature of one of the catalyst components (an aluminium trialkyl) and the expense involved in removing the catalyst components from the polymerized olefin, at least one company in the oil industry carried out a programme of work in which various transition metal salts, dissolved in alkane solvents, were irradiated in the presence of ethylene or propylene with the consequent formation of polymeric materials.[2]

No report of this type of work has appeared in the scientific literature and it was considered worthwhile to institute an investigation of the system with a view to its possible development as an economically feasible process operating at near ambient temperatures and at atmospheric pressure.

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EXPERIMENTAL

Materials

Cylinder ethylene from the British Oxygen Company or the British Hydrocarbon Chemicals was passed through a purification train designed to remove oxygen, acetylene, carbon monoxide, carbon dioxide and water. The final dessicant was P_2O_5. Phillips Research Grade ethylene was only dried.

Propylene was obtained from Matheson Co. (C.P.) and from Sherman Chemicals Co. (99·9 per cent). The propylene was de-aerated on a vacuum line using either liquid nitrogen or acetone–CO_2 as coolant, and dried by passing it through a P_2O_5 tube in the vacuum line.

Heptane (technical grade) was treated repeatedly with cold concentrated sulphuric acid until no further discolouration of the acid occurred, then washed, dried and finally distilled under dry nitrogen over sodium using a 10-theoretical-plate column. The fraction with b.p. 98·5 $\pm$ 2·0°C was collected.

B.D.H. Reagent grade $TiCl_4$ was used initially without further treatment, but later it was purified according to the method of CLABOUGH *et al.*[3] which was designed to ensure removal not only of metallic impurities such as vanadium but also carbonaceous materials, e.g. carbonyl chloride and chlorinated organic compounds.

Radiation sources

A Co^{60} source of 175 c and 4 MeV linear accelerator was used. With an annular reaction vessel the dose rate from the Co^{60} source was initially 0·21 Mrad/hr, whereas using the electron beam from the accelerator the estimated dose rate was about 60 Mrad/hr. In the first case ferrous sulphate solution was used for dosimetry; with the accelerator the dose was estimated from the known power of the beam at the sample position and corrected for the wall thickness of the reaction vessel.

Irradiation procedure; Co^{60} *source*

The annular reaction vessel, fitted with a spiral glass stirrer and, at the bottom, a glass sinter for introduction of the gas, was baked out at 200°C *in vacuo* and filled with the $TiCl_4$–heptane mixture in a dry box under an atmosphere of dry oxygen-free nitrogen. Prior to irradiation the vessel was flushed with ethylene. The gas pressure was always kept just above atmospheric pressure by venting excess gas through a water cooled condenser and a drying tube. Flow rates were measured with a rotameter.

For irradiations using propylene, an all-glass pump was used to circulate the gas around a closed system at atmospheric pressure. The dose rate in the spherical reaction vessel was about half that obtained in the annular vessel.

Irradiation procedure, 4 MeV *electron accelerator*

A 500 ml round-bottom three-neck flask was used. Phillips Research Grade ethylene was passed over P_2O_5 before entering the flask below the liquid surface. Rapid stirring was employed and the vessel was cooled with water directed against the side facing the electron beam. Propylene was de-aerated and dried as described above and the storage vessel kept at about −25°C while allowing the propylene to expand through a needle valve into the reaction vessel. Flow rates were not measured but the gases were passed into the solution at rates estimated to be in excess of that required for saturation.

Estimation of polymer

After irradiation, the solution was quenched with methanol, and the polymer suspended in the heptane was washed with further portions of methanol or acetone. After filtration or centrifugation the solid was vacuum dried. In some cases ether was used to remove oily products.

The average molecular weight of polyethylene was determined viscometrically at 105·0°C using xylene as solvent in a suspended-level viscometer. An expression relating intrinsic viscosity to $\bar{M}_w$ due to TREMENTOZZI[9] was used, in the form

$$[\eta] = 1{\cdot}65 \times 10^{-4}(\bar{M}_w^{0{\cdot}83}).$$

RESULTS

Co^{60} *gamma rays on ethylene*

No polymer was obtained with B.O.C. or B.H.C. ethylene used directly from the cylinders or only dried. Using the whole purification and drying train, comparable yields of polymer were obtained from both grades. Phillips research grade ethylene was not used with this source.

The amounts of polymer obtained per unit energy input were widely scattered, probably due to residual impurities, and a systematic variation with changes in original ethylene supply, ethylene flow rate (up to 100 ml/min at N.T.P.), dose rate, total dose or $TiCl_4$ purity could not be detected. The average yield, calculated in terms of the amount of ethylene converted to solid polymer per unit energy input to the 1 per cent solution of $TiCl_4$ in heptane was $G(-C_2H_4) = 22$ molecules per 100 eV, at 25·0°C.

At 45·0°C $G(-C_2H_4)$ was reduced to 7; at 65·0°C negligible amounts of polymer were produced. No work was done below room temperature.

4 MeV *electrons on ethylene*

Using Phillips research grade ethylene, either straight from the cylinder or only passed over P_2O_5, an average of $G(-C_2H_4) = 35$ was obtained. The increase over that obtained with Co^{60} gammas is not significant as the dose rate from the accelerator was not accurately known and experimental variation was very large in each case.

A significant increase in $G(-C_2H_4)$ was obtained by increasing the $TiCl_4$ content to 10 per cent vol./vol., and values of 102 and 105 were found in two experiments.

For both methods of irradiation, polyethylene molecular weights (weight average) varied from 8000 to 12000 but not systematically with variables such as radiation source, $TiCl_4$ concentration, etc.

Propylene polymerization

No polypropylene was obtained using the Co^{60} source and recirculating flow system.

With 4 MeV electrons only one of nine experiments yielded appreciable solid polymer and even in this case $G(-C_3H_6)$ was only 2·6. This experiment also yielded a relatively large amount of oil with $G(-C_3H_6)$ about 80. Other experiments yielded some oil but no solid polymer. In all these experiments the initial solutions were from 1 to 10 per cent vol./vol. $TiCl_4$ in heptane.

DISCUSSION

There is some evidence that the lower valency states of titanium are necessary for olefin polymerization. In BP 777538[5] it is stated that $TiCl_3$ is ineffective for converting propylene to solid polymers but that the dichloride is an effective catalyst. In BP 778639,[6] issued to the same company, the same claim is made with respect to ethylene polymerization and an example is given in which 1·5 g of solid polyethylene was obtained using 2·7 g of $TiCl_2$ in cyclohexane at 195–197°C and an ethylene pressure of 1000 lb/in². However, this was a very low yield compared with other examples given in the same patent in which various complexes of $TiCl_4$ with metal alkyls were used. In Belgian Patent 553478[7] are described the polymerization of ethylene using $TiCl_3(CH_3)$ and mixtures of $TiCl_3(C_2H_5)$ with $TiCl_3$ as catalysts. LUDLUM *et al.*[8] have reported that the activity of catalysts produced by the reaction of $TiCl_4$ with aluminium or lithium alkyls depends on the valency state of the Ti in the complex, with two the optimum valency. It appears to be the function of the aluminium alkyl to reduce and then alkylate the titanium.

It is therefore considered that the irradiation of a $TiCl_4$–heptane mixture causes decomposition of both components followed by the formation of lower valency alkyl titanium compounds—probably chlorides.

The compounds thus formed include various valency states and differing degrees of alkylation. The alkyl radicals may be expected to contain from one to seven carbon atoms. Some of the compounds may be relatively good catalysts. This situation is far removed from that existing with typical Ziegler catalyst systems in which a relatively large amount of a more uniform catalyst is present. Therefore, when a $TiCl_4$–heptane solution is irradiated a multiple catalyst system is produced, but the proportion of effective catalyst may be small, and since the effective catalyst, being of low valency, is most likely to be destroyed by oxidizing impurities, it is evident that a higher degree of purity is required than is necessary with normal Ziegler catalysts. This would be particularly necessary at low dose rates.

The large amount of low molecular weight oily product obtained with propylene agrees with the result obtained by the Esso Company.[2] RASUWAJEW *et al.*,[9] using $TiOCl_2$ as a catalyst, obtained low molecular weight products with propylene. This indicates a possible connexion between oxygen contamination of the monomer and low yields of solid polymer.

The yields of polyethylene obtained in this work were closely similar to those calculated from data in the Esso patent.[2]

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Ionization Current Measurement of Aqueous Solutions Containing C^{14}

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Reproducible ionization current measurement of aqueous solutions containing C^{14} can be achieved by standardizing the sample position and thickness, and eliminating or reducing evaporation. A brief comparison is made with other methods used in the measurement of soft β-emitters in aqueous solution and the advantages of ionization current measurement are outlined.

MESURE DU COURANT D'IONISATION DANS LES SOLUTIONS AQUEUSES CONTENANT C^{14}

On peut arriver à des courants d'ionisation reproductibles dans le dosage du C^{14} en solution aqueuse en étalonnant la position et l'épaisseur de l'échantillon et en éliminant ou diminuant l'évaporation. Cette méthode est comparée brièvement avec d'autres servant au dosage des émetteurs de rayonnement β-mou en solution aqueuse et les avantages de celle-là sont exposés.

ИЗМЕРЕНИЕ ИОНИЗАЦИОННОГО ТОКА В ВОДНЫХ РАСТВОРАХ, СОДЕРЖАЩИХ C^{14}

Воспроизводимые результаты измерения ионизационного тока в водных растворах, содержащих C^{14}, могут быть получены стандартизацией положения и толщины образца и исключением или снижением испарения. Дается краткое сравнение других методов, применяемых для измерений в случае мягких бета-лучей в водных растворах и описываются преимущества измерений ионизациноного тока.

DIE IONISATIONSSTROMMESSUNG IN WÄSSERIGEN, C^{14} ENTHALTENDEN LÖSUNGEN

Reproduzierbare Ionisationsstrommessungen in wässerigen C^{14} Lösungen können bei Eichung der Lage und Schichtdicke der Probe und Vermeidung oder Verminderung der Verdampfung erzielt werden. Einige Methoden, die für die Bestimmung von Isotopen, die weiche β-Strahle aussenden, in wässeriger Lösung benützt werden, sind einem kurzen Vergleich unterzogen mit gleichzeitiger Beschreibung der Vorteile der Ionisationsstrommessung.

INTRODUCTION

In biochemical tracer work, the need for assaying labile aqueous solutions containing C^{14} or other weak β-emitters for radioactivity is frequently encountered. Until recently this has generally involved evaporating off the water and either counting the dried residue as such or, more often, converting this material to $BaCO_3$, CO_2 or to some other form suitable for Geiger–Müller (G–M) counting. Apart from being time consuming, such procedures may also have the disadvantage that the samples required for assay cannot be recovered unchanged for further study.

Recent developments in G–M[1,2], proportional[3] and scintillation[4,5] counting have made possible the assay of weak β-emitters in aqueous solution under certain

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conditions. An earlier G–M method was not recommended for accurate measurement,[1] but latest advances[2] have led to improvements in both design and sensitivity. Present trends appear to make this the method of choice where continuous flow systems, such as chromatographic eluates, are under investigation. With the proportional counting technique,[3] up to 10–15 per cent of water can be tolerated in the counting medium before insulation breakdown occurs. No information on the absolute sensitivity is available, but the method has been recommended only for highly active samples. Sample recovery is possible by the choice of a suitable solvent mixture; formamide for instance would permit protein recovery. On the other hand, liquid scintillation counting is perhaps the most promising from the point of view of sensitivity,[6] even though the counting efficiency is reduced by water itself and by some of the agents which are usually required to give homogeneous solutions with scintillators. However, some of the suggested solvent mixtures may be unsuitable for certain biochemical work, because both the counting and the subsequent recovery of solutions may be difficult in some systems. Thus, the addition of ethanol as recommended in one procedure[7] could result in the formation of precipitates from aqueous solutions containing protein. Even with alternative techniques[4] there are still a number of problems which have not been entirely overcome. Coloured or opaque solutions, which are frequently encountered in biological work, present one such difficulty in scintillation counting, namely that of quenching.

Recent improvements in electrometer design, which have paralleled the above developments, have been reviewed by TOLBERT[8,9]. With the equipment now available, the range of measurable currents in the ionization chamber has been extended to much lower levels than had hitherto been possible. Ionization currents are measured with maximal efficiency in the gaseous phase, but by simple modification of the ionization chamber it is possible to assay aqueous solutions at a somewhat reduced efficiency.[10] This latter means of assay is essentially window-less and at least as sensitive as the latest G–M method,[2] although not potentially as sensitive as liquid scintillation counting (Table 1). However, the measurement of ionization currents does overcome some of the problems associated with the scintillation technique.

TABLE 1. Relative sensitivities of the techniques used for the radioassay of aqueous solutions

Isotope	Minimum radioactivity measurable (μc/ml)		
	Liquid scintillation counting*	Ionization current measurement†	G–M counting‡
C^{14}	3×10^{-5}	5×10^{-3}**	1×10^{-2}
H^3	2×10^{-4}	2×10^{-1}	—

* From Reference[6], after allowing for the sample size and for the reduced efficiency of the water-containing scintillating solution, as suggested by the author.

† From Reference[10].

‡ From Reference[2].

** In the present work a figure of 1×10^{-2} was obtained (Table 4) but the ultimate limit may not have been reached.

In assaying liquids in an ionization chamber, attention must be paid to the geometry of the sample and to the effects due to volume changes brought about by evaporation in particular. It is the purpose of this paper to give more detailed consideration than has been given so far[10] to the special precautions which must be taken to ensure a reproducible ionization current measurement of aqueous solutions containing C^{14}.

EXPERIMENTAL

A Nuclear Chicago model 6000 Dynacon Electrometer equipped with a DCL slide chamber was used in these investigations. A 90 V battery-supplied polarizing potential was applied to the chamber. A stainless-steel sample pan with a surface area of 100 cm^2 provided by the manufacturers and aluminium planchets made locally with

areas of 5·1 and 1·0 cm^2 were used for mounting the radioactive solutions. The radioactive solutions were prepared by suitably diluting 1 mc glycine-2-C^{14} (supplied by the Radiochemical Centre, Amersham, U.K.) with distilled water and these were stored in the frozen state. A 15 min period was allowed for equilibration before current measurement. Measurements were performed in air with vents open to prevent condensation of liquid within the chamber; this inevitably raised the background current on account of the radon in the air, and resulted in some loss of sensitivity. Currents of 10^{-13} A and higher were measured by the high-resistance-leak method, while those of 10^{-14} A and under by the rate-of-charge method. In the 10^{-14} A region either method was used interchangeably, depending on the particular requirements of the experiment. A chart recorder was used throughout.

RESULTS AND DISCUSSION

Position effects

The need for a centering device for sample pans of areas smaller than 100 cm^2 was established in experiments with a C^{14}-impregnated strip of perspex mounted on a 5·1 cm^2 planchet. Table 2 shows that, in the absence of a centering device, maximal ionization currents are obtained from a centrally placed source. To ensure reproducibility some sort of centering device is therefore desirable, but at the same time such a device should not be too bulky, otherwise the ionization current is also reduced. A Y-shaped piece of 24 gauge aluminium was thus found to be a more satisfactory device than the 70 cm^3 metal cylinder supplied with the chamber. The corresponding background currents are similarly influenced to some extent by the volume of the centering device, but these effects are very much smaller.

With solutions it was found that samples of smaller surface area (but otherwise equal in C^{14} content and thickness) gave rise to higher ionization currents, presumably because of the concentration of the source towards the centre of the chamber (Table 3).

Evaporation effects

In liquid measurements one of the factors influencing the ionization current is the evaporation of water from samples. When large volumes such as 10 ml are involved, the amount of evaporation in the course of the usual measuring time is so small as to be almost negligible (Table 3), but with decreasing volumes this effect becomes very much more accentuated. The current increase was found to be linear, at least up to 24 hr when a 10 ml or 1 ml solution was introduced into the chamber. With 100 μl the linearity was maintained for only about 3 hr and was followed by a much steeper rise in the ionization current. The dry sample eventually gave a reading of 1·91 $\times$ 10^{-12} A.

It has previously been suggested[10] that evaporation could be controlled by addition of sufficient phosphoric or sulphuric acids to give a final concentration of 50 per cent

TABLE 2. Influence of the source position and of the centering device on the ionization current obtained from a solid C^{14} source

Centering device		Background ionization current (A $\times$ 10^{-16})	Source position	Ionization current in presence of source (A $\times$ 10^{-13})
Description	Volume (cm^3)			
None	—	6·6	Central	1·29
			Peripheral	1·06
			Intermediate	1·23
Y-shaped Al	0·7	5·4	Central	1·23
Metal cylinder	70·0	0·6	Central	0·93

TABLE 3. Effects of geometry and evaporation on the ionization currents obtained from C^{14}-glycine solutions containing 1 μc

Solvent	Volume (ml)	Area (cm^2)	Thickness (cm)	Ionization current* ($A \times 10^{-14}$)	Increase in ionization current due to evaporation† (A/hr)
H_2O	10·0	100·0	0·100	3·65	$3·1 \times 10^{-16}$
	1·0	5·1	0·196	2·11	$1·35 \times 10^{-15}$
	0·1	1·0	0·100	5·18	$2·90 \times 10^{-14}$
H_2O/glycerol	1·0	5·1	0·196	1·83	$2·7 \times 10^{-16}$
	0·1	1·0	0·100	4·46	$4·40 \times 10^{-15}$

* Extrapolated to zero time, not corrected for background.

† These figures are subject to alteration by prevailing atmospheric conditions.

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by volume. While this procedure is not suitable for use with aluminium pans, glycerol at a similar concentration was found to be almost as effective as phosphoric acid in reducing the vapour pressure. Even if non-corrosive pans were used, glycerol would still be preferable in some other studies where acidification may have to be avoided, such as those involving volatile labelled organic acids, e.g. acetic acid.

Density changes are known to influence the counting efficiency of β-emitters in solution,[11] and it is therefore not surprising to find that the addition of glycerol results in an overall decrease in the ionization current by a factor of about 1·16 as compared to water. The observed increase in the ionization current due to evaporation from the 50 per cent glycerol solution was linear for a 1 ml solution, but in the case of a 100 μl solution the linearity was again only maintained for about 3 hr. After this time a gradual slowing down of the rate of current increase was observed and finally a stable value was established in the vicinity of $7·3 \times 10^{-14}$ A.

The background currents measured in presence of water or 50% glycerol were subject to considerable fluctuation usually between 6 and 8×10^{-16} A and occasionally as high as $1·6 \times 10^{-15}$ A. The fluctuations were such that any current changes due to changes in the volume of water were not detectable.

Thickness effects

The effects of evaporation and of the sample geometry reported in Table 3 suggest an inverse relationship between the thickness of the aqueous solution and the ionization current. However, more direct information on this aspect was clearly desirable.

When the total activity of the sample and the surface area were held constant at 1 μc and 100 cm^2 respectively, then an increase in volume (and thickness) resulted in a drop of the ionization current as indicated in Fig. 1. It would obviously be advantageous to spread volumes smaller than 5 ml over an area of 100 cm^2, if this were practicable. However, even with 5 ml solution, it was necessary to add a larger volume (10–15 ml) at first, and then make careful withdrawls to avoid a break in the surface.

When the concentration of the C^{14}-glycine was kept constant at 1 μc/ml with the surface area again at 100 cm^2, then the ionization current dropped off linearly with increasing volume (thickness and total radioactive content), as shown in Fig. 2. From the Figure it can be calculated that for such a solution the ionization current decreases by $3·3 \times 10^{-15}$ A for each additional millilitre of solution. For a 0·1 μc/ml solution a figure of $3·8 \times 10^{-16}$ A/ml is arrived at, while the values for currents extrapolated to zero volume are $4·06 \times 10^{-13}$ and $4·06 \times 10^{-14}$ A, respectively.

C^{14} *assay*

The above observations emphasize the need to standardize on volume, area and solvent composition for the assay of aqueous

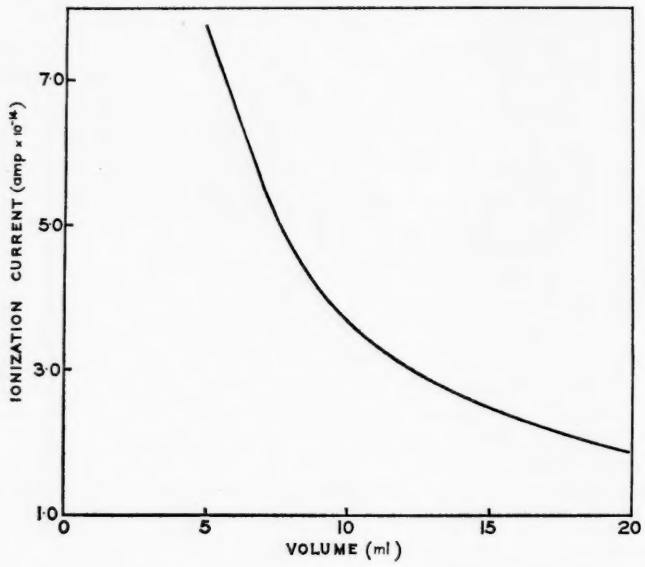

FIG. 1. Effect on the ionization current of varying volumes of water added to 1 μc C^{14}-glycine. Not corrected for the background current. Surface area, 100 cm².

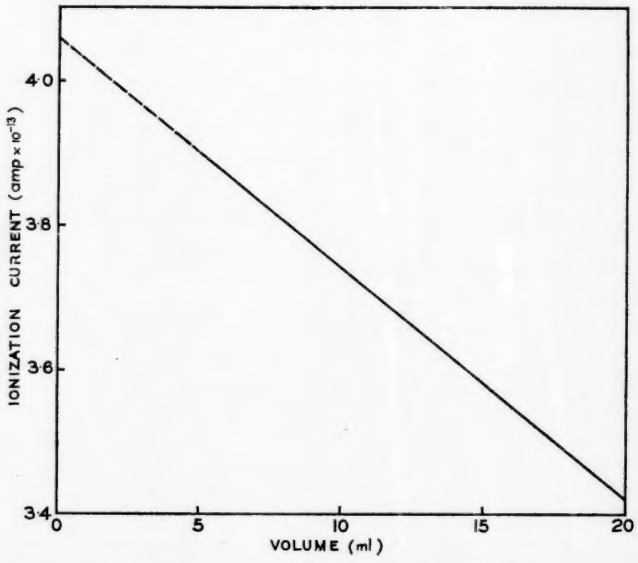

FIG. 2. Effect on the ionization current of varying volumes of a 1 μc/ml solution of C^{14}-glycine. Not corrected for the background current. Surface area, 100 cm². The extrapolation to zero volume is shown by the broken line.

solutions. When this is done, the ionization current becomes directly proportional to the C^{14} content of the sample (Table 4). At the lowest concentration level the accuracy is only ± 10 per cent, since it is subject to the fluctuations already referred to in connexion with the background current. It is not claimed however, that the ultimate limit has necessarily been reached in this work, since more precise measurements at the 10^{-15} A level may be possible, but sufficient accuracy and reproducibility has been achieved for the present purposes. Some improvement might be achieved by temperature control and by elimination of the current surges which are caused by transients on the power line and which could not be suppressed even when an harmonically filtered constant-voltage transformer was used.

CONCLUSION

TABLE 4. Ionization currents obtained from serially diluted C^{14}-glycine solutions in 10 ml water with a surface area of 100 cm^2

Concentration (μc/ml)	Ionization current (A)	
	Observed	Corrected*
10·00	$3{\cdot}61 \times 10^{-12}$	$3{\cdot}61 \times 10^{-12}$
1·00	$3{\cdot}66 \times 10^{-13}$	$3{\cdot}65 \times 10^{-13}$
0·10	$3{\cdot}65 \times 10^{-14}$	$3{\cdot}57 \times 10^{-14}$
0·01	$4{\cdot}4 \times 10^{-15}$	$3{\cdot}6 \times 10^{-15}$

* Corrected current = observed current less background current (8×10^{-16} A).

On the basis of the present findings it is recommended that attention should be paid to the following factors.

(1) The procedure should be standardized for a constant volume and surface area. If use of a constant volume of solution is not possible, extrapolation to zero volume may be resorted to.

(2) A maximum surface area consistent with the sample volume should be used.

(3) Samples with surface areas smaller than that of the tray should be centered by means of a compact device.

(4) Changes in volume due to evaporation in small volumes of liquid (under 10 ml) can be minimized by the addition of glycerol. If in the subsequent recovery of the solution such an addition is undesirable or if less than 1 ml liquid is being handled, then the ionization current should be extrapolated to zero time.

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A Simple Method of Estimating the Tritium Content of Biological Samples

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A quick and simple method of sample preparation is described for the determination of tritium in biological samples by liquid scintillation counting. It involves combustion by copper oxide alone in expendable pyrex glass envelopes and can be used for up to 100 mg of sample.

The method is applicable to wet or dry tissues or to radioactive solutions; for tissue powders it is found to give linear and reproducible results and tests of overall efficiency indicate that losses are not more than 5 per cent.

The liquid scintillation counter used is of original design and has an efficiency of approximately 10 per cent.

UNE MÉTHODE SIMPLE POUR LE DOSAGE DU CONTENU DE TRITIUM DANS LES ÉCHANTILLONS BIOLOGIQUES

On décrit une méthode rapide et simple de préparer les échantillons pour le dosage du tritium dans les échantillons biologiques dans un compteur à scintillement liquide. Elle entraîne la combustion par l'oxyde de cuivre seul dans des enveloppes de verre pyrex qui sont dépensables et qui peuvent servir pour jusqu'à 100 mg d'échantillon.

La méthode s'applique aux tissus mouillés ou secs, ou bien aux solutions radio-actives; pour les tissus en poudre on trouve qu'elle donne des résultats reproduisibles et linéaires, et des expériences sur l'efficacité totale indiquent que les pertes ne dépassent pas 5 pour cent.

Le compteur à scintillement liquide utilisé est de forme originale et possède une efficacité d'environ 10 pour cent.

ПРОСТОЙ МЕТОД ОПРЕДЕЛЕНИЯ СОДЕРЖАНИЯ ТРИТИЯ В БИОЛОГИЧЕСКИХ ОБРАЗЦАХ

Описан простой и быстрый метод отбора проб для определения трития в биологических образцах с пмощью жидкого сцинтилляционного счетчика. Метод заключается в окислении на окиси меди в пирексовой трубке и может быть применен для проб в 100 мг.

Метод применим к влажным и сухим тканям или к радиоактивным растворам. Найдено, что для измельченных в порошок тканей получаются линейные зависимости и воспроизводимые результаты, а при испытании на общую эффективность потери не превышают 5%.

КПД жидкгоо сцинтилляционного счетчика оригинальной конструкции составляет 10%.

EINE EINFACHE METHODE ZUR BESTIMMUNG DES TRITIUMGEHALTES IN BIOLOGISCHEN PROBEN

Es wird eine einfache und schnelle Methode zur Herstellung von Proben beschrieben, welche zur Tritiumbestimmung in biologischen Proben mittels flüssiger Szintillatoren verwendet werden. Die Methode kann für 100 mg Proben angewendet werden und besteht in

der Verbrennung zusammen mit Kupferoxyd in einem einmalig verwendbaren Pyrexglasrohr. Sie kann für frische und getrocknete Gewebe und für radioaktive Lösungen angewandt werden. Für pulverisierte Gewebe wurden lineare und reproduzierbare Ergebnisse erhalten und eine Überprüfung der erhaltenen Ausbeuten zeigt, dass die Verluste nicht mehr als 5 % betragen. Ein gewöhnlicher Szintillations-zähler wurde verwendet, seine Ausbeute betrug ungefähr 10 %.

I. INTRODUCTION

THE liquid scintillation counting technique is now becoming established as the standard method for the routine assay of tritium. It was developed in the hope that involved sample preparation would normally be unnecessary, the sample being dissolved directly in the detecting medium and measured with 4π geometry and good efficiency. In some cases this is possible, but more often simplicity is lost because of the difficulty of dissolving reasonable quantities of most materials in the available liquid scintillators.

Biological tissues present a special problem in tritium assay, firstly because of their heterogeneous nature and secondly because they contain substances of high molecular weight and sparing solubility in most solvents. The difficulties of getting whole tissue into a non-quenching solution in a toluene-based scintillator are not insuperable, however, and a number of workers claim to have done this. When working satisfactorily such methods appear to be both rapid and simple, and in cases where a large number of samples of the same tissue have to be measured they are probably unsurpassed. Nevertheless, as the papers in Reference[1] show, solution methods are not entirely straightforward. Colouring of the scintillator and phosphorescence effects have been reported and no paper yet published states clearly which tissues can and which cannot be dissolved (presumably bone cannot). There appears to be some justification for an alternative method, especially one which can be applied immediately to biological samples of any description.

The one described here is a highly simplified dry combustion procedure. It enables a sample of wet or dry tissue to be prepared and measured within $\frac{1}{2}$ hr reliably and accurately using simple and inexpensive apparatus.

II. THE COPPER OXIDE COMBUSTION–DISTILLATION METHOD

(1) *Outline of the method*

The method is briefly as follows: the sample of tissue is intimately mixed with black copper oxide and heated in one end of an expendable pyrex glass combustion tube whilst the other end is maintained at −65°C in a freezing bath (Fig. 1). Complete combustion takes place producing water and carbon dioxide, and the water, containing all the tritium from the sample, distils to the cool end of the tube. The combustion tube is then broken beyond the limit of condensation and the tritiated water washed out into a volume of liquid scintillator with sufficient absolute ethanol to form a stable ternary solution. The combustion tube may be made in either of two ways. For weights of dry sample not exceeding 50 mg the tube may simply be sealed off and used as a closed system. With larger sample weights the system can be operated at atmospheric pressure by forming a U-tube condenser at its lower end. The former method is the simplest and has been used for well over 300 assays. The latter method enables up to 100 mg of dry sample to be used, but requires more care in producing controlled combustion.

Some elaboration of the technique is necessary, for as described it is unsatisfactory in the two following respects.

(a) Volatile samples or volatile products of partial combustion distil away from the combustion zone before being completely burned.

(b) The yield is only about 80 per cent

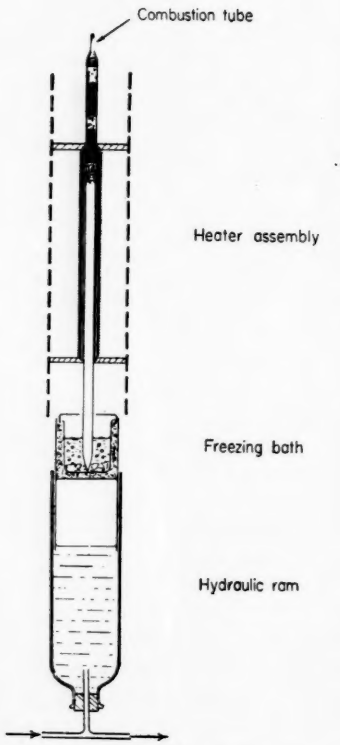

FIG. 1. The combustion–distillation system.

for 15 min combustion time, though it may be increased by prolonged heating.

Two simple developments have eliminated these shortcomings and enabled complete combustion to be achieved within 10 min.

(2) *The three-zone combustion tube*

To eliminate the first of these sources of error a column of about 1 g of pure copper oxide is inserted between the combustion zone and the region of condensation and is preheated to red heat, thus providing an effective trap for unburned gases from the sample.

The second source of error appears to be due to the time taken for residual water vapour to diffuse down the tube and be condensed. A "scavenger" is therefore needed and a convenient technique is to introduce about 0·1 g of a 1 : 10 glucose–copper oxide mixture beyond the sample combustion zone and to heat this when sample combustion is complete. The inactive water produced sweeps out any residual active water vapour and ensures complete collection.

The developed combustion tube thus has three reaction zones: the vapour trap, sample combustion column and scavenger zone. The mixing of dry tissue powders with copper oxide is straightforward: wet tissue specimens must first be ground with solid carbon dioxide and then combined with copper oxide below freezing point. Liquid samples are introduced first into $\frac{1}{4} \times \frac{3}{4}$ in. carrying tubes partly filled with copper oxide; these are then filled with more copper oxide and quickly dropped into the prepared combustion tube.

The tube itself is of pyrex glass tubing 10–11 mm o.d. and 50 cm in length. Prior to filling, one end is drawn out to a sharp but not-too-fragile point (after combustion using the enclosed tubes this is heated in a bunsen flame to vent the carbon dioxide pressure); the three reaction zones are then formed and separated by loose plugs of glass wool, "Analar" cupric oxide being used throughout.

Care must be taken not to compact the two main copper oxide zones during filling and to make the final glass wool plug sufficiently substantial, otherwise part of the tube filling may migrate during combustion and possibly move out of the heater.

(3) *The combustion apparatus*

The heating of the three-zone combustion tube is carried out using a single heating coil as follows. The tube is first inserted so that the upper end of the heater, which is already hot, bisects the first (vapour trap) column of copper oxide and the lower end of the tube rests in the freezing bath. This is then steadily lowered allowing the combustion tube to fall through the heater at a rate of about 1 in./min until the upper tip of the tube enters the heater and all three zones are heated; finally the system is held in this position until the time from the start of combustion is at least 10 min. A simply constructed hydraulic ram, which can be lowered steadily and at an adjustable rate

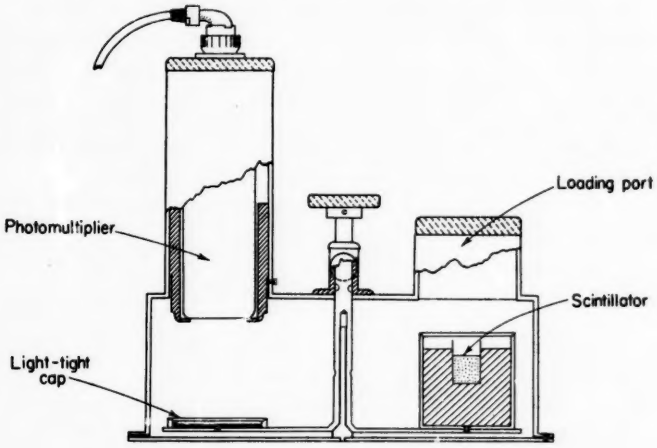

FIG. 2. Diagram of the liquid scintillation counter.

by means of a controlled leak, enables the movement of the bath to be accomplished conveniently and reliably. The body of the ram is a cylindrical glass jar with a single feed-pipe at the bottom connected via a two-way tap either to the water main for filling or to a constricted rubber tube to give the controlled leak.

The float consists of an open-ended cylinder of thin copper sheet fitting easily within the glass jar. It has a soldered air-tight partition which divides an upper container for the freezing bath and cotton wool insulation from the lower air-filled space which gives the buoyancy. A freezing mixture consisting of 20–30 ml of methylated spirits in equilibrium with pieces of solid carbon dioxide has been found suitable.

The heater consists of an $8\frac{1}{2}$ in. pyrex glass former, 0·7 in. o.d., on which is wound 60 ft of 24 s.w.g. heating coil wire ("Brightray C" H. Wiggin & Co. Ltd.). It is fed from the a.c. mains and an 8 A "Variac" is used to give the required operating temperature of about 650°C. Two disks of $\frac{3}{16}$ in. asbestos sheet are clamped to the ends of the former and these support an expanded-metal guard.

(4) *Brief outline of the counting method used*

Radioactivity measurements were carried out using a liquid scintillation counter of original design (Fig. 2). The scintillator is contained in cylindrical aluminium tubes of up to 50 ml capacity; these can be inserted into a solid aluminium holder and brought close underneath the photocathode of a 2 in. photomultiplier (E.M.I. 9514 "S") by a revolving turntable. The turntable also carries a light-tight cap which prevents over-exposure of the photomultiplier when the turntable is raised for sample changing. The whole counter is operated in a deep-freeze at −26°C. Since the counter is made entirely of metal parts it is free from the troublesome phosphorescence effects which arise in glass scintillator containers. In addition a good efficiency for tritium is obtained without a coupling fluid between scintillator and photocathode: the aluminium tubes as manufactured have a highly reflecting but uneven surface which is just what is required for a minimum amount of light trapping within the scintillator.

Tritiated water samples resulting from the combustion procedure are washed out into the aluminium counting tubes using first two washings of 1·0 ml absolute ethanol and then one with 3·0 ml of 0·3 % diphenyloxazole in "Analar" toluene. The scintillator thus consists of 40 % alcohol and at −26° it will hold at least 0·2 ml of water. Under these conditions a counting efficiency of about 10 per cent is obtained, with a background of about 10 c.p.s.

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Because of the sensitivity of the tritium counting efficiency to such factors as the degree of optical coupling, amount of tritiated water and electronic parameters, each sample when counted is calibrated by the addition of a non-quenching internal standard and recounting. A suitable sub-standard consists of 0·5 per cent tritiated water in absolute ethyl alcohol (4 μc/ml). It is kept in a sealed micro-syringe and added in 20 μl volumes.

Since the counting tubes are non-phosphorescent, samples may be recounted immediately after insertion in the counter. The counting and combustion procedures thus fit together excellently: one sample is measured and calibrated during the combustion period of the next.

III. EVIDENCE FOR THE INTEGRITY OF THE METHOD

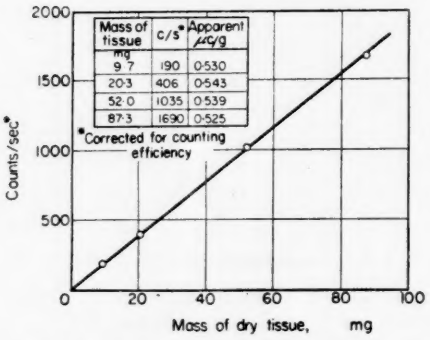

FIG. 3. The reproducibility of dry tissue assay.

(1) *The linearity and reproducibility of dry tissue assay*

A single sample of mixed dry tissue was used from animals which had been sacrificed at various periods after the injection of 25 μc of tritiated thymidine. The excized tissues were shredded, dried over phosphorous pentoxide and then powdered.

The results (Fig. 3) show excellent linearity and reproducibility: the standard deviation of the values of specific activity deduced from these measurements is 1·3 per cent of their mean. This is rather better, though, than is usually observed, 3 per cent being more common.

(2) *Measurements of overall efficiency*

A direct measurement of overall combustion efficiency may be made for any tritium-labelled sample which can also be reliably measured by an independent method. In the case of liquid samples this has been done by comparing the counting rates due to two 20 μl volumes of the sample, one of which is subjected to combustion and the other used as an internal standard. This has been done using tritiated water and also with an alcoholic solution of tritiated thymidine (each about 4 μc/ml). When water was used, 50 mg of inactive dry tissue powder was added to each sample for combustion, following the view of WILZBACH[2] that this is to some extent a test of the combustion efficiency of the tissue powder. The overall efficiency has also been checked using solid tritiated thymidine. In this case the true activity of the sample was determined by a solution method involving the use of "Hyamine" hydroxide.[3] Table 1 lists the results of these tests: each value is the mean of five measurements.

(3) *Variation of yield with sample particle-size*

There is a danger that since the combustion reaction takes place in the solid state it may be largely a surface reaction, failing to remove tritium entirely from the centre of a particle of tissue. If this is so, a study of the effect of particle-size and hence of reacting surface should reveal it.

Liver samples from two animals which had been sacrificed at 15 and 30 min after an injection of 25 μc of tritiated thymidine

TABLE 1

	Combustion efficiency (%)	Standard deviation (%)
H^3 water with tissue	99·6	3·5
H^3 thymidine in ethanol	99·4	2·3
Solid H^3 thymidine	95·1	3·9

were shredded, dried over phosphorous pentoxide and powdered. Then, using 200, 100, 60 and 40 mesh standard wire sieves, the powder was divided into five ranges of particle-size and each was assayed for tritium content. The results gave a standard deviation of 7 per cent of the mean with a slight tendency to rise with increasing particle size. This can only be attributed to some correlation of tritium content with particle size.

IV. CONCLUSION

The copper oxide combustion–distillation method is presented as a simple and reliable technique of tritium sample preparation for liquid scintillation counting. When used with tissue specimens it is found to give linear and reproducible results and in so far as it has been possible to measure the overall efficiency it has been found to be at least 95 per cent.

In addition, the experience of over 300 assays has shown that the system is very convenient in use and is pleasantly independent of factors such as the weights of copper oxide used and the combustion time.

Acknowledgements—Whilst acknowledging the advice and help of many of my colleagues in the Institute of Cancer Research, I would especially like to record my thanks to Dr. L. F. LAMERTON and Professor W. V. MAYNEORD for valuable discussions; also to Mr. M. PHILLIPS for his skill in the construction of the counter.

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Determination of Fe^{55} and Fe^{59} in Blood

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The simultaneous use of the two radio-iron isotopes (Fe^{55} and Fe^{59}) available today offers distinct advantages in studies on iron absorption and metabolism. The greatly differing energy of radiation from these isotopes makes the precision of the double isotope analysis dependent on both the preparation of the sample and on the counting system.

As a result of studies on both these steps a method is described in detail.

The determinations are performed on electroplated samples in a gas-flow counter using beryllium and platinum absorbers. The method has given very satisfactory results in studies on the absorption and metabolism of iron in humans.

DETERMINATION DE Fe^{55} ET Fe^{59} EN SANG

L'emploi ensemble des deux radio-isotopes de fer à présent disponibles (Fe^{55} et Fe^{59}) donne des avantages nets pour l'étude de l'absorption et la métabolisme du fer. La grande différence d'énergie du rayonnement de ces isotopes rend l'exactitude du double dosage isotopique dépendante et de la préparation de l'échantillon et du système de comptage.

On décrit ici une méthode en détail, à la suite d'une étude de ces deux aspects.

Les dosages se font dans un compteur à écoulement de gaz avec des échantillons électroplaqués, en employant des absorbants de glucinium et de platine. La méthode a rendu de très bons résultats dans des recherches sur l'absorption et sur le métabolisme du fer chez l'homme.

ОПРЕДЕЛЕНИЕ Fe^{55} И Fe^{59} В КРОВИ

При исследовании поглощения и обмена железа определенное преимущество имеет одновременное использование двух радиоизотопов железа (Fe^{55} и Fe^{59}), доступных в настоящее время. Так как энергии излучения этих изотопов весьма различны, то точность двойного изотопного анализа зависит как от приготовления образца, так и от системы счета. В результате исследования этих двух вопросов дано дательное описание метода. Определения производились на гальванизированных образцах в газовом счетчике с применением бериллиевых и платиновых поглотителей. Метод дает очень хорошие результаты при исследовании поглощения и обмена железа у человека.

BESTIMMUNG VON Fe^{55} UND Fe^{59} IM BLUT

Die gleichzeitige Verwendung der beiden heute erhältlichen radioaktiven Eisen-Isotope (Fe^{55} und Fe^{59}) bieten bedeutende Vorteile bei Untersuchungen von Eisen-Absorption

und-Stoffwechsel. Die stark differierende Energie der Strahlung dieser beiden Isotope macht die Genauigkeit der doppelten Isotopen-Analyse sowohl von der Preparation der Probe wie vom Detektor abhängig.

Eine Methode welche diese beiden Umstände berücksichtigt wird ausführlich beschrieben.

Die Messungen wurden an elektrolytisch hergestellten Proben in einem Gas-Durchlaufzähler durchgeführt, wobei Be- und Pt-Absorber verwendet wurden. Die Methode führte zu sehr befriedigenden Resultaten bei Untersuchungen über menschlichen Eisenstoffwechsel und Aufnahme.

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In biological and medical investigations, a more adequate experimental design can very often be achieved by the use of two or more isotopes of the same element simultaneously or by labelling different atoms of the same compound with different isotopes. This is particularly true in kinetic problems when a substance may be exchanging with several body compartments.

In studies on iron absorption and metabolism, the simultaneous use of the two radio-iron isotopes (Fe^{55} and Fe^{59}) available today may offer distinct advantages. However, we have found difficulties in the analysis of the two isotopes in a single sample, employing previously published methods.

The greatly differing energy of radiation from the two isotopes and the very weak radiation from Fe^{55} makes the precision of the double isotope analysis dependent on both the preparation of the sample and on the counting system. Both steps are studied in this paper and the results obtained form the basis for the described method.

The present status of methodology is only briefly summarized. The method most extensively used was devised by PEACOCK *et al.*[1], to determine separately Fe^{55} and Fe^{59} in mixtures. In this method the blood sample was digested, the iron precipitated as the hydroxide, redissolved in acid and electroplated on copper planchets. Using two Geiger tubes with different window material and different gas fillings, the sensitivity of the two tubes for Fe^{55} and Fe^{59} were different, thus allowing determinations of the two isotopes from the same planchet. However, the efficiency of counting of Fe^{55} by this method is less than 1 per cent. Recently DERN[2] described a method where a higher efficiency could be obtained by the use of liquid scintillation counting. However, as mentioned in that paper, other sources of considerable error were introduced which may interfere with the practical application of this method. Moreover, a considerable crossover of Fe^{59} radiation to the Fe^{55} peak was obtained which may decrease the accuracy of determinations of Fe^{55} when a sample contains much Fe^{59} and little Fe^{55}.

Determinations have also been made using a Geiger tube preferentially sensitive to Fe^{55} (electroplated sample) and a scintillation well crystal counter sensitive only to Fe^{59} (liquid sample).[3] The absence of cross counting from Fe^{55} in the Fe^{59} detecting system will usually not outweigh the advantage of measuring both isotopes in the same sample as in the two earlier methods.

Owing to weakness of its radiation, Fe^{55} can only be measured from electroplated samples or by a liquid scintillation system. Determination of Fe^{55} in the presence of Fe^{59} can be done from electroplated samples using either Geiger tubes as described by PEACOCK *et al*[1], or proportional gas-flow counters fitted with suitable filters or scintillation counters with very thin crystals. As suitable photomultiplier tubes were not available at the start of this work, we did not succeed in separating in thin crystals the radiation of Fe^{55} from the radiation of Fe^{59}. However, an increased efficiency of counting of Fe^{55} was obtained with a proportional gas-flow counter using a suitable counting gas mixture and suitable filters.

Electroplating of iron is thus a necessary step for most methods of determining Fe^{55}. Using earlier-described methods[6–9] for the electrodeposition of iron, it was very hard to achieve sufficient accuracy for our purposes and very often an appreciable and unpredictable loss of activity occurred. For this

reason the factors influencing the electrodeposition of iron have also been studied.

As a result of these investigations a method of electroplating and counting has been devised which has been in constant use for more than 2 years and which offers distinct advantages over earlier-described methods.

EXPERIMENTAL

I. *Electroplating of Iron*

To study factors which may influence the electrodeposition of iron the kinetics of this process was studied using Fe^{59} as a tracer. By adding 0·5–1 μc of Fe^{59} to the electrolyte containing inert iron, less than 1 per cent of the original amount of iron in the electrolyte can easily be determined in a scintillation well crystal. The rate of electrodeposition under different conditions has been determined by transferring at different times the electrolyte quantitatively to a volumetric flask from which four millilitres are taken for analysis in the well counter and compared with a standard solution prepared from the original solution added to the electrolyte.

Electrolysis cell

The design of the electrolysis cell and the anode was found to influence greatly the deposition of iron.

To obtain an even distribution of the electrodeposited iron, either the ratio between the anode–cathode distance and the diameter of the cathode had to be large or the diameters of the anode and cathode had to be of the same magnitude. A large anode–cathode distance increases the resistance of the cell and thus increases the temperature of the solution and of the cathode, and dark soft plates will result. On the other hand, a large anode will interfere with the circulation of the electrolyte and thus also with the electrolytic deposition of iron. Designing the anode as a rotating propeller or using a nitrogen bubbler improved the mixing but not sufficiently to get reproducible results using cells as described by Peacock *et al.*[1]. We also found that the local heating of the cathode interfered with the quality of the electrodeposit.

On the basis of these studies, an electrolysis cell was constructed with good anode–cathode geometry, adequate mixing without mechanical devices and with a heavy steel base with a considerable heat capacity. The cell was also designed for ease of handling. It is made of acid resistant stainless steel and acrylate plastic (Fig. 1). The heavy base has a polished surface on which the copper planchet is placed. A rubber O-ring is used as a gasket between the planchet and the top part of the cell. A bayonet-catch assures the tightness of the cell.

The anode is a platinum spiral with a diameter of 2 cm, melted into a pyrex glass tube filled with mercury. In the set-up used twenty-four cells are coupled in series to secure the same current through all cells. The current is regulated with a rheostat. The anode–cathode distance is about 2 cm which gives a voltage across each cell of 4–5 V at a current of 0·4 A at the start of the electrolysis.

Factors influencing the electrodeposition of iron

The main factors determining the rate of electrodeposition of iron are current density, pH of the solution, temperature and circulation in the electrolyte. The more acid the solution the less iron is deposited. The greater the hydroxyl-ion concentration in the solution, the more the risk of formation of a ferric hydroxide precipitate. When ammonium salts of organic acids are used, for instance ammonium oxalate which form complex compounds with iron, the solubility product of ferric hydroxide will not be exceeded. This is because not only will ferric ion concentration be depressed but the hydroxyl ion concentration also, because of the low dissociation of ammonium hydroxide. The hydroxyl ion concentration can be still more

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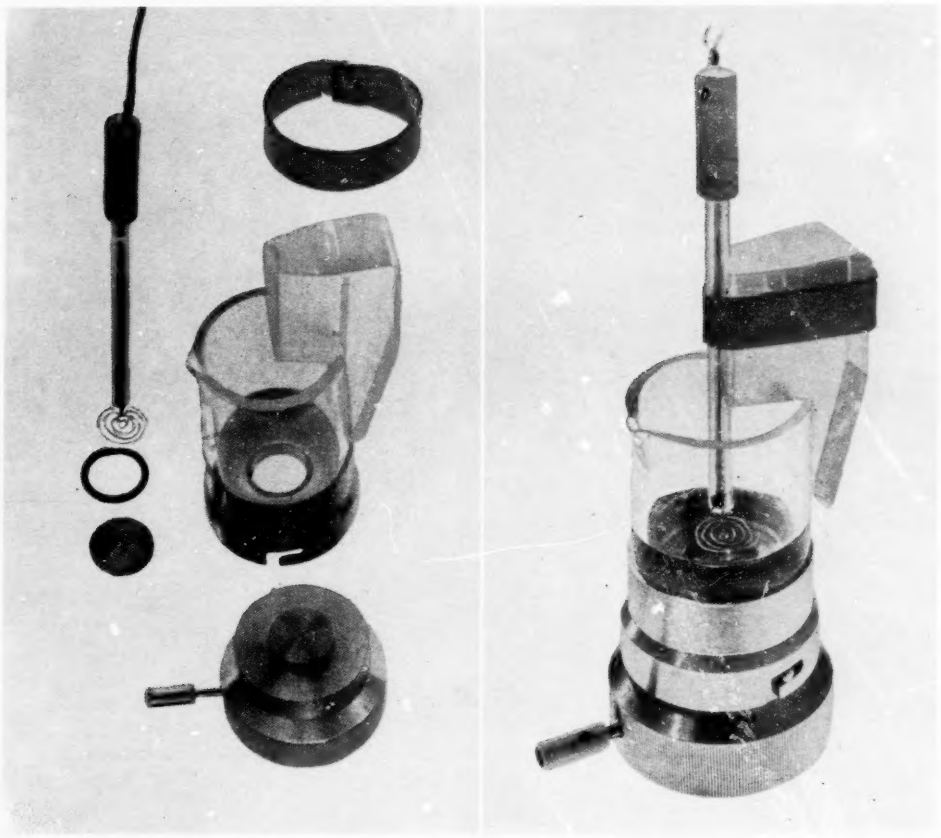

FIG. 1. Electrolysis cell. To the left are the different parts of the cell and to the right is the cell mounted and filled with electrolyte.

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decreased by the addition of more ammonium ions.

The composition of the electrolyte will thus greatly influence the rate of electrodeposition and the solubility of iron in the electrolyte. With 5 mg of iron we have found that 25 ml of a saturated ammonium oxalate solution is sufficient to avoid precipitation of ferric hydroxide. An excess of ammonium oxalate has usually been used (35 ml) and more ammonium ions in the form of ammonium sulphate (Table 1) have been added to decrease further the hydroxyl ion concentration in the electrolyte.

When the amount of iron is greater than 5 mg the composition of the electrolyte has been modified to prevent precipitation of ferric hydroxide. By increasing the amount of ammonium oxalate as well as the amount of ammonium sulphate, the exceeding of the solubility product of ferric hydroxide will be avoided. The varying amounts of ammonium oxalate and ammonium sulphate used with varying amounts of iron are shown in Table 1. The amount of 6 N sulphuric acid initially used to dissolve the ferric hydroxide precipitate in the centrifuge tubes with varying amounts of iron is also included in Table 1.

TABLE 1. The amount of sulphuric acid used to dissolve the iron hydroxide precipitate and the amounts of ammonium oxalate and ammonium sulphate in the electrolyte at different amounts of iron

	Amount of iron (mg)				
	2·5	5	7·5	10	12·5
Sulphuric acid (ml)	1·2	1·2	1·6	2·0	2·4
Ammonium oxalate (ml)	35	35	45	50	55
Ammonium sulphate (ml)	2	2	3	4	6

The rate of electrodeposition of iron with varying amount of iron in the electrolyte initially is shown in Fig. 2 using a current of 0·375 A. In these experiments the composition of the electrolyte is the same as in Table 1.

After 4 hr less than 1 per cent of the initial amount of iron (2·5 and 5 mg) is left in the electrolyte. At this time about 2 per cent is left when electroplating 10 mg of iron.

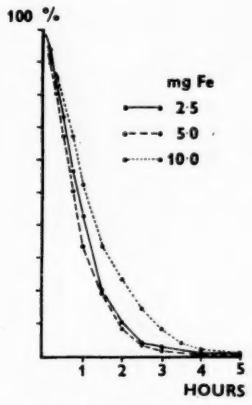

FIG. 2. Rate of electrodeposition of varying amounts of iron at 0·375 A.

The effect of varying the current has been studied with the same amount of iron (5 mg) and the results are shown in Fig. 3.

Using a current of 0·7 A, the maximum amount of iron electroplated is found at about 2 hr. After this time, there is a tendency for the electroplated iron to redissolve.

On the basis of these studies, the electroplating technique has been standardized in the following way: 5 mg of iron are electroplated for 4 hr at a current of 0·4 A.

Preparation of blood samples and standards

Digestion. Heparinized blood samples or blood drawn in ACD-solution (e.g. 150 ml blood in 50 ml ACD-solution containing 1·32 g of sodium citrate, 0·48 g citric acid and 1·47 g glucose diluted to 100 ml with water) were haemolysed by freezing and thawing. This facilitates the quantitative pipetting of blood in the following step. Using a long calibrated pipette the amount of blood corresponding to 5 mg of iron is delivered into a 250 ml Kjeldahl flask to which 10 ml of concentrated sulphuric acid is added. The iron content of the blood–ACD sample is calculated from a haemoglobin determination using the cyanmethemoglobin method.[4]

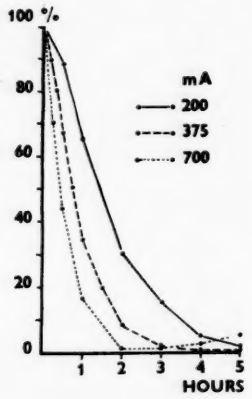

FIG. 3. Rate of electrodeposition of 5 mg iron at varying currents.

The specimen is digested with sulphuric acid for 2 hr. Three to four millilitres of 60% perchloric acid are added when the solution is cool. The specimen is then boiled to water clearness. After cooling, the solution is transferred to a 150 ml centrifuge tube. The flask is thoroughly rinsed with small portions of distilled water until the rinse water is no longer acid (litmus paper). All rinse water is also transferred to the centrifuge tube. The solution is neutralized with concentrated ammonium hydroxide (25%) using bromcresol purple as indicator. After cooling, the precipitate is brought down by centrifugation and the clear supernatant is removed by slow and careful suction.

The precipitate is dissolved in 1·2 ml of 6 N sulphuric acid and is allowed to stand for 20 min and if necessary another few drops of sulphuric acid are then added. Two millilitres of a 50% ammonium sulphate solution is then added.

Electroplating. The 1 in. copper planchets are washed one by one in 30% nitric acid until nitrous oxide fumes are formed. The planchets are then washed in distilled water and mounted in the electrolysis cell.

The dissolved iron precipitate is quantitatively transferred from the centrifuge tube to the cell together with 35 ml of ammonium oxalate solution (saturated and filtered at room temperature) and the electrolysis is started immediately. Before mounting, the electrodes are mechanically adjusted to secure a constant anode–cathode geometry. The electrode distance is 2 cm and the current through the cell 0·4 A. After exactly 4 hr the electroplating is interrupted. The planchets are immediately rinsed in distilled water, dipped in 96% ethyl alcohol and dried with an electric hair fan.

Washing. To avoid radioactive contamination, all glassware is immersed overnight in dilute hydrochloric acid containing about 1 per cent iron. The glass is then washed several times in tap water and finally in distilled water. Glassware used for standards of Fe^{55} and Fe^{59} are never interchanged and never used for ordinary analyses. The electrolytic cells and the platinum electrodes are washed immediately after use and are also soaked in dilute hydrochloric acid.

Recovery experiments

The total loss of iron during the digestion and electroplating procedure has been determined using Fe^{59} as a tracer. Five milligrams of biologically labelled haemoglobin iron was digested and electroplated as described. The plates were dissolved in nitric acid and the activity measured in a scintillation counter and compared with the original blood sample. The average recovery of sixteen experiments was 95 $\pm$ 0·9 per cent.

In the same way the recovery of 5 mg of inorganic iron was studied in sixteen experiments and found to be 94 $\pm$ 1 per cent.

These studies were performed on planchets selected at random from actual measurements of standard solutions and blood samples during a period of 3 months.

As all calculations are based on comparisons with standard solutions treated in the same way as the unknown samples, the loss of iron during the procedures does not interfere with the accuracy of the method, as this loss is very constant and of the same magnitude for blood samples and standard solutions.

II. *Analysis of* Fe^{55} *and* Fe^{59}

As was mentioned in the introduction, a suitable gas-flow counte operated in the

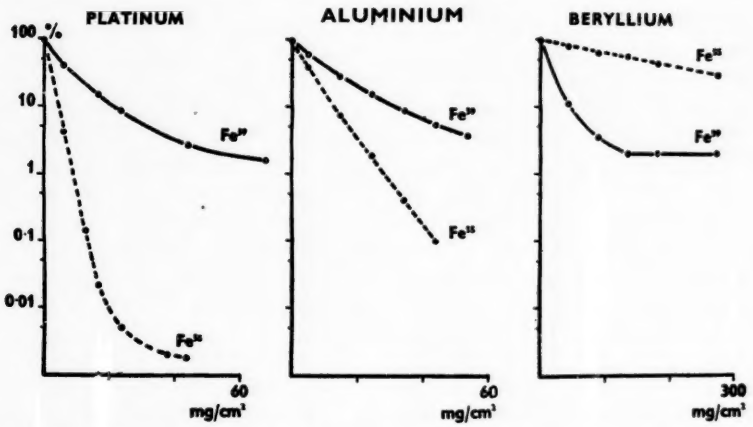

FIG. 4. Transmission of radiation from Fe^{55} and Fe^{59} in platinum, aluminium and beryllium.

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proportional region was found to give higher efficiency than a Geiger tube which had been used earlier.

In our studies we finally selected a commercial gas-flow counter with a micro-thin mylar window mounted in an automatic sample changer.*

Absorption of Fe^{55} *and* Fe^{59} *in platinum, aluminium and beryllium*

The absorption of β-radiation is mainly determined by the energy of the radiation and the mass of the absorber. The absorption of X-radiation is in addition and to a great extent also influenced by the atomic number of the absorbing material. These facts were utilized by PEACOCK *et al.*[7] in designing the Geiger tubes for measuring Fe^{55} and Fe^{59}.

To obtain the optimal conditions for measuring Fe^{55} and Fe^{59} in mixtures with the gas-flow counter, we studied the absorbing qualities of materials with greatly differing atomic numbers. The results are shown in Fig. 4

The X-radiation from Fe^{55} was absorbed by platinum ($z = 78$) to a very great extent and the ratio of the absorption of Fe^{55}/Fe^{59} was much higher in this material than in aluminium ($z = 13$) with its lower atomic number In beryllium ($z = 4$) the absorption of Fe^{55} is much smaller than the absorption of Fe^{59}. With a 0·75 mm beryllium absorber, 45 per cent of the radiation of Fe^{55} is absorbed as compared to 98 per cent of the radiation of Fe^{59}.

The unchanged absorption of Fe^{59} with increasing thickness of the beryllium absorber when the absorber is thicker than 0·75 mm is probably due to interaction of the γ-radiation with the metallic wall of the detector. With another construction of the detector it might be possible to reduce this effect and to increase the Fe^{55}/Fe^{59} transmission ratio with a thicker beryllium absorber.

With a 0·011 mm platinum absorber, only 0·005 per cent of the radiation from Fe^{55} will be transmitted. From a practical point of view the Fe^{55} radiation in this system can be disregarded when the relative amounts of the two isotopes in a sample are of about the same magnitude. With this platinum absorber 8·8 per cent of the Fe^{59} radiation will be transmitted.

Measurements and calculations

Standard samples of Fe^{55} and Fe^{59} and unknown samples containing the same amount of iron are measured three times with a beryllium filter and with a platinum filter to a constant number of counts (usually three times 3000 counts) in the automatic sample changer. A counting gas of 10 per cent of pure methane in argon is used. To avoid leakage into the counter

* Baird Atomic Inc., Cambridge, Mass., U.S.A.

an overpressure of 2 cm of silicone oil is used. In this system a plateau between 2100 and 2500 V with a slope of less than 1 per cent is obtained. From the observed net counts per minute of the standard samples and the unknown samples with the two absorbers, the Fe^{55} and Fe^{59} content of the unknown samples can be determined using the same equations as have been applied to analysis of two isotopes with gamma spectrometry with two energy channels (see for instance ÖBRINK and ULFENDAHL[5]).

However, using 0·75 mm of beryllium and 0·011 mm of platinum absorbers much simpler calculations can be used as the counts from Fe^{55} can be neglected when using a platinum absorber of this thickness.

Simple arithmetic will give:

$$S_{Be}^{55} = S_{Be} - S_{Pt} \cdot \frac{St_{Be}^{59}}{St_{Pt}^{59}},$$

where

S_{Be}^{55} = Fe^{55} net counts in unknown sample with beryllium absorber.
S_{Be} = net counts of unknown sample with beryllium absorber.
S_{Pt} = net counts of unknown sample with platinum absorber.
St_{Be}^{59} = net counts of standard sample with beryllium absorber.
St_{Pt}^{59} = net counts of standard sample with platinum absorber.

The Fe^{55} content of an unknown sample is obtained from the calculated S_{Be}^{55} and the net counts of the standard sample of Fe^{55} using the beryllium absorber. The Fe^{59} content of an unknown sample is directly obtained from the observed net counts of the standard sample of Fe^{59} and the unknown sample using the platinum absorber.

Efficiency

With the described systems 1 μc Fe^{59} gives $1{\cdot}1 \times 10^5$ counts/min with the platinum absorber and $2{\cdot}0 \times 10^4$ counts/min with the beryllium absorber. Of Fe^{55} 1 μc will give $1{\cdot}2 \times 10^5$ counts/min with the beryllium absorber and less than 30 counts/min with the platinum absorber.

The background with the beryllium or the platinum absorber varies between 10 and 15 counts/min.

Compared with the system described by PEACOCK *et al.* the efficiency for counting Fe^{55} is increased about seven times.

To study the possibilities of increasing the practical efficiency by increasing the amount of sample (i.e. increasing the amount of electroplated iron) varying amounts of iron were plated together with a constant amount of Fe^{55} and Fe^{59}, respectively.

The results are shown in Fig. 5. By plating 10 mg of iron instead of 5 mg from the same blood sample, the efficiency can be

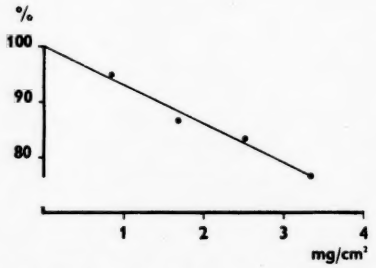

FIG. 5. Relative efficiency of counting Fe^{55} together with varying amounts of inert iron.

increased by 70 per cent which is of importance in samples with low activity. Using planchets with greater diameter it is of course possible to increase the practical efficiency $\left(\frac{(\text{net counts})^2}{\text{background}} \text{ in relation to the dose administered}\right)$ still further.

Experimental error of the method

The precision and accuracy of the method has been studied in different ways and different sources of error have been analysed statistically.

(1) *Accuracy of the method.* Known amounts of Fe^{55} and Fe^{59} have been digested together with 5 mg of inert iron, precipitated, dissolved and electroplated in the usual way. The counts obtained have been expressed as a percentage of the counts expected, and will thus be an expression of the systematic

error (accuracy) of the method. The relationship between Fe^{55} and Fe^{59} will be an indirect expression of the precision of the method. The results are shown in Table 2.

TABLE 2. Accuracy of the method

Parts in the mixture		Found in percentage of expected		
Fe^{55}	Fe^{59}	Fe^{55}	Fe^{59}	Fe^{55}/Fe^{59}
1	1	98·4	99·1	0·99
1	1	98·1	98·6	0·99
1	1	102·9	100·8	1·02
1	1	99·6	98·2	1·01
	Mean	99·8	99·2	1·00
1	2	98·9	98·5	1·00
1	2	99·1	97·7	1·01
1	2	99·3	97·8	1·02
1	2	100·7	99·2	1·02
	Mean	99·5	98·3	1·01
2	1	99·6	99·3	1·00
2	1	94·9	96·0	0·99
2	1	96·4	97·0	0·99
2	1	96·4	98·8	0·98
	Mean	96·8	97·7	0·99

(2) *Precision of the method.* From planchets selected at random, the precision of the method has been calculated. Six standard samples from each of four different standard solutions during a period of 3 months have been determined. In this way twenty-four Fe^{59} samples and twenty-four Fe^{55} samples have been analysed. The coefficient of variation of a single planchet has been calculated and the results are shown in Table 3.

The precision of determinations of Fe^{55} and Fe^{59} in blood samples has been calculated from twenty-four planchets selected at random, from series where four samples were electroplated from the same blood sample. Six groups of four samples were analysed statistically and the coefficient of variation of a single planchet is also given in Table 3.

TABLE 3. Precision of the method

	Standard samples		Blood samples	
	N	V %	N	V %
Fe^{55}	4 × 6	±2·3	6 × 4	±3·0
Fe^{59}	4 × 6	±3·1	6 × 4	±3·6

A resolution of the experimental error in different steps showed that the variation between series digested and electroplated on different days was six times smaller than the variation within one series, which means that samples analysed on different days can be compared without introducing any great additional error. This will also mean that it is not necessary to include standard samples in each digestion and electroplating series. However, we have always done this as a safety precaution.

III. *Summary*

A method for the determination of Fe^{55} and Fe^{59} is described in detail. The determinations are performed on electroplated samples in a gas-flow counter using beryllium and platinum absorbers. Factors influencing the electrodeposition of iron are analysed using Fe^{59} as a tracer. The design of the electrolysis cell is studied and a convenient cell facilitating the quantitative electrodeposition is described. On the basis of these studies the electroplating technique is standardized.

The absorption of the radiation of Fe^{55} and Fe^{59} in different materials is studied, employing the gas-flow counter. Two absorbers giving optimal discrimination between the two isotopes were selected in the final design of the method. With a 0·75 mm beryllium absorber, 55 per cent of the Fe^{55} radiation is transmitted but only two per cent of the Fe^{59} radiation. With a 0·011 mm platinum absorber 8·8 per cent of the Fe^{59} radiation is transmitted but only 0·005 per cent of the Fe^{55} radiation.

The method has been used in studies on iron absorption and iron metabolism in humans and has given very satisfactory results.[10–13]

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The Destruction of *Salmonella* Bacteria in Refrigerated Liquid Whole Egg with Gamma Radiation

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Thermal pasteurization being a borderline process, it was attempted to use ionizing radiation for rendering whole egg, intended for preservation by other methods than freezing, free from *Salmonelleae*. Initial densities of about 10^7/ml of *S. typhimurium* and *S. senftenberg* were used. Irradiation was carried out with a ca. 1500 c Co^{60}-source, the inoculated whole egg being packed in lacquered tins and kept at ca. 1°C during this treatment.

Six decimal reductions of the *Salmonella*-species tested were obtained at dosages of 2×10^5 rad, nine reductions at slightly over 5×10^5 rad. No effect of the use of specific recovery media or pre-treatments on the apparent dose value required for obtaining these reductions could be established.

The odour of the whole egg and its functional properties appeared to have been impaired at dosages of 10^4 rad, while the colour suffered from ca. 2×10^5 rad. Therefore, the radiation pasteurization of liquid whole egg at ca. 1°c cannot be considered a promising process.

LA DESTRUCTION DE LA BACTÉRIE *SALMONELLE* DANS L'OEUF ENTIER LIQUIDE RÉFRIGÉRÉ AU MOYEN DU RAYONNEMENT GAMMA

Vu que la pasteurization thermique est un procédé marginal, on essaya l'emploi du rayonnement ionizant pour rendre libre de *Salmonellae* l'oeuf entier destiné à la conservation par autres moyens que le gel. On utilisa des densités initiales d'environ 10^7/ml. de *S. typhimurium* et de *S. senftenberg*. Le rayonnement se fit avec une source de Co^{60} d'environ 1500 c, l'oeuf entier inoculé étant enfermé dans des boîtes métalliques laquées, et maintenu à environ 1°C durant ce traitement.

Six diminutions décimales des espèces de *Salmonella* mises à l'essai furent obtenues pour des doses de 2×10^5 rad, et neuf diminutions pour un peu plus de 5×10^5 rad. On ne put établir aucun effet sur la valeur de dose apparente nécessaire pour donner ces diminutions, que pourrait rendre l'emploi des agents spécifiques de rétablissement ou des traitements préalables.

Il y avait une détérioration apparente de l'odeur de l'oeuf entier et de ses qualités fonctionnelles à des doses de 10^4 rad, et un changement de couleur à partir d'environ 2×10^5 rad. Ainsi on ne peut guère considérer comme une méthode de promesse la pasteurization au rayonnement de l'oeuf entier liquide à environ 1°C.

УНИЧТОЖЕНИЕ *Salmonella* БАКТЕРИИ В ОХЛАЖДЕННОМ ЦЕЛОМ ЖИДКОМ ЯЙЦЕ ПРИ ПОМОЩИ ГАММА-ОБЛУЧЕНИЯ

Для уничтожения *Salmonella* в целых яйцах, хранение которых производится не в холодильниках, были сделаны попытки применить ионизирующее излучение, поскольку термическая пастеризация является неизбирательным процессом. Исходные концентрации *S. typhimurium* и *S. senftenberg* были 10^7/мл. Облучение производилось источником Co^{60} мощностью ~1500 кюри, причем зараженное яйцо помещали в жестяную запаянную банку и выдерживали при ~1°C в течение всего опыта.

Шесть десятикратно разбавленных образцов, зараженных *Salmonella* были подвергнуты облучению дозами в 2×10^5 рад, а девять образцов–дозами немного выше 5×10^5 рад. Применяемая питательная среда и предварительная обработка не влияли на величину дозы, требующейся для указанных разбавлений.

Дозы в 10^4 рад вызывали появление запаха и меняли функциональные свойства целого яйца, а дозы в 2×10^5 рад приводили к изменению окраски. Следовательно, применение радиационной пастеризации целого жидкого яйца при ~1°C следует признать бесперспективным.

DIE VERNICHTUNG VON SALMONELLA BAKTERIEN IN GEKÜHLTER EIFLÜSSIGKEIT MIT HILFE VON γ-STRAHLUNG

Da thermale Pasteurisierung hier nicht angewendet werden kann, wurde versucht, Eier, für die andere Konservierungsmethoden als Tiefkühlung vorgesehen waren, durch ionisierende Strahlung von Salmonella zu befreien. Als Ausgangskonzentration wurde etwa 10^7/ml von S. Typhimurium und S. Senftenberg verwendet. Die Bestrahlung wurde mit Hilfe einer etwa 1500 C Co-^{60}-Quelle durchgeführt. Die infizierten Eier wurden in gelackte Dosen verpackt und während der Behandlung auf ca. 1°C gehalten.

Eine Verminderung um 6 Grössenordnungen der Zahl der untersuchten Salmonella-Spezies wurde durch eine Dosis von 2×10^5 rad erreicht, während eine Verminderung von 9 Grössenordnungen bei etwas über 5×10^5 rad eintrat. Die Verwendung von speziellen Wiederbelebungsmitteln und Vorbehandlungen ergaben keine Veränderungen des Dosiswertes, der zur Erzielung der erwähnten Verminderung nötige war. Der Geruch und die funktionellen Eigenschaften der Eier wurden bei Dosen von 10^4 rad beeinträchtigt, während Farbenveränderungen bei ca. 2×10^5 rad auftraten. Die Pasteurisierung von Eiflüssigkeit durch Bestrahlung bei 1°C kann daher nicht als eine günstige Methode betrachtet werden.

It seems to be well established now, that the future use of ionizing radiation in the processing of fresh perishable foods, if any, will be limited to low dosage treatments, especially pasteurization and disinfestation.[8]

Because the thermal pasteurization of liquid whole egg, being a typical borderline process, continues to present occasional problems, it was considered worthwhile to carry out a few tentative tests on the possibilities of using ionizing radiation for this purpose. The irradiation of frozen whole egg has been rather well studied;[2,13] therefore in the present study it was specifically attempted to irradiate liquid egg under refrigeration, as it seems hardly practicable to pre-freeze liquid eggs for pasteurization purposes prior to preservation methods other than freezing.

At the same time it was investigated whether Alper and Gillies's observation that a strain of *Escherichia coli*, carrying radiolesions, was better recovered in slightly unfavourable media than in commonly used optimal ones[7] was also valid for *Salmonelleae* irradiated in foods.

EXPERIMENTAL DETAILS

Raw material

Fresh hens' eggs were washed with 0·5% chloramine solution, thereupon broken out and the yolks and whites obtained mixed under aseptic conditions. The product so obtained was immediately cooled to about 2°C. It had an aerobic and anaerobic plate count of less than 10^2 organisms/1 ml.

Adequate portions of this material were inoculated with *Salmonella typhimurium* and *S. senftenberg* in initial densities of about 10^7/ml. The first strain was chosen because it is one of the most important causes of human salmonellosis in The Netherlands,[4] the latter because rather heat-resistant varieties of this serotype have been encountered in the United States.[1] The rather high initial densities were considered necessary to allow a sufficient safety margin for the opportunities which may exist in egg-breaking plants for a few *Salmonella*-infected hen's eggs to contaminate rather large amounts of whole egg and for the subsequent considerable increase in numbers of *Salmonelleae* in such lots.[2,3]

The refrigerated inoculated material was

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canned in lacquered tins, measuring ca. 7 × 1·5 cm and kept at about 2°C throughout subsequent procedures.

Irradiation

Irradiation was carried out in the Department of Radiology, Municipal Hospitals, The Hague, under the direction of Mr. H. R. Marcuse, Health Physicist. The source used consisted of about 1500 c Co^{60}-fuel rods.

In order to be able to irradiate at a continuous range of dosages, cans containing inoculated egg were stacked to a height of about 50 cm and transferred to an aluminium container, maintained at 0–1°C. Cans irradiated at a level of ca. 10^4, 3×10^4, 1×10^5, 2×10^5 and 5×10^5 rad were used for further investigation. Radiation at this level required about 10 hr exposure to the γ-source.

During the experiments the temperature in the whole egg never exceeded 2°C.

Bacteriological examination of irradiated samples

Irradiated samples were examined both by enrichment in liquid media and by direct counts in solid media using optimal as well as selective media.

The enrichment media were brain heart infusion broth, MULLER's tetrathionate broth[12] and OSBORNE and STOKES's selenite bile brilliant green sulphapyridin medium.[14] About 30 g of the irradiated material was both directly seeded into these media and after 1 hr incubation in nutrient broth at 37°C, followed by 6 hr further incubation in nutrient broth, to which 5 μg/ml of chloramphenicol had been added.[7] Enrichment cultures so obtained were further examined in the usual way.[10]

The solid media used were crystal violet neutral red bile lactose mannitol agar,[9] nutrient agar and TDYM-agar.[11] These media were again seeded both with the freshly irradiated samples of whole egg and with material having been pre-incubated in nutrient broth plus chloramphenicol at 37°C. Adequate proportions of colonies obtained in plates were confirmed as *Salmonelleae* in the usual way.[10]

General examination of irradiated samples

The freshly irradiated samples were also tested for taste, odour, colour and for significant colloidal properties. The latter were assessed by carrying out a dispersion test, in which 5 ml of whole egg is gently shaken with 45 ml of water and thereupon allowed to settle. In this assay, untreated whole egg forms a copious sediment, while irradiated samples of liquid egg show very much less sediment and more complete dispersion, the latter increasing with the dose of radiation to which the samples have been subjected.

RESULTS

Judged by the results of the method of direct plate counts, "total inactivation", which implies reduction from ca. 10^7 to <10/ml, of all *Salmonelleae* was obtained at dosages of 2×10^5 rad. No significant influence of media or pre-treatments on the recovery of irradiated cells could be detected in these experiments.

Based on the outcome of enrichment tests, reduction from ca. 10^7 to $<10^{-2}$ viable *Salmonelleae* per 1 ml of whole egg, required dosages of at least 5×10^5 rad. Because this dosage was the highest one tested, complete inactivation of *Salmonelleae* was not attained in a few of the tests. Here again, no consistent effect of the use of specific

TABLE 1. Relative radiation resistance of the strains of *S. typhimurium* and *S. senftenberg* tested

Dose of γ-radiation (rad)	Numbers of surviving cells of	
	S. typhimurium	*S. senftenberg*
0	$0{\cdot}6 \times 10^7$	$0{\cdot}6 \times 10^7$
10^4	$0{\cdot}8 \times 10^7$	$0{\cdot}9 \times 10^5$
3×10^4	$0{\cdot}1 \times 10^7$	$0{\cdot}2 \times 10^4$
1×10^5	$0{\cdot}7 \times 10^3$	$0{\cdot}05 \times 10^2$
2×10^5	<10	<10
5×10^5	<10	<10

media or pre-treatments could be established. The strain of *S. senftenberg* tested appeared to be less radiation resistant than the strain of *S. typhimurium*, as the figures in Table 1 show. These differences did not, however, materially influence the doses of radiation required in practice for inactivation.

General examination of the irradiated samples showed that the odour of all materials had been impaired already at dosages of 10^4 rad. Colloidal changes also became obvious at this dosage, while colour impairment occurred invariably at 2×10^5 rad, and in some tests even at lower dosages.

DISCUSSION OF RESULTS

The bactericidal effects of γ-radiation on *Salmonelleae* observed in the present investigation are in good agreement with those obtained by NICKERSON *et al.*[13]. The fact that BROOKS and colleagues in Britain found lower inactivation doses for *Salmonella* in eggs[2] seems quite obvious in view of the very much lower initial density (ca. 10/ml vs. 10^7/ml in the American and our assays) used by that group.

We have been unable to find any influence of the post-irradiation medium on the recovery of irradiated *Salmonelleae* analogous to that described by ALPER and GILLIES for *E. coli* strain B. Our findings are thus in agreement with the general conclusions of DAVYDOFF[5] and FREEMAN and BRIDGES[6] who investigated other species.

The denaturation effects which were encountered in our experiments were more serious than those observed by both NICKERSON *et al.* and BROOKS *et al.* This is most probably due to the fact that we deliberately carried out irradiation at $+1°C$ not ca. $-20°C$ and also used high doses. The off-flavours noticed will most probably have little effect on the taste of baked goods, although they may exert a detrimental influence on the flavour of pastry fillings; while the international egg products trade, where judgement of lots is based on the flavour of the *raw* merchandise, would have to be duly informed if radiation pasteurization might become a reality. The observed loss of colloidal ("functional") properties of irradiated whole egg will most probably affect the quality of baked goods.

Our conclusion must therefore be that radiation pasteurization of liquid whole egg, refrigerated but not frozen, cannot be considered a promising process.

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Compartmentalized Phantoms for the Standard Man, Adolescent and Child*†

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A compartmentalized phantom for the standard man has been designed and built of readily available and inexpensive materials. Similar phantoms have also been designed for an adolescent and a child. The basic emphasis in the designs is on general utility so that a variety of different dose-measurement techniques could be used on the same phantom. The designs are, however, in reasonable agreement with anthropometric data reported in the literature. The phantoms have proved to be extremely useful in depth dose and energy-absorption measurements for total-body irradiation therapy. Dose measurements with beam teletherapy, brachytherapy devices and internally distributed radioisotopes have also been made.

DES FANTÔMES COMPARTIMENTÉS POUR L'HOMME NORMAL ET POUR L'ADOLESCENT ET L'ENFANT

Un fantôme compartimenté pour l'homme normal a été dessiné et construit de matériaux facilement disponibles et peu coûteux. On a également dressé des plans pour les fantômes comparables d'adolescent et d'enfant. L'insistance fondamentale dans les dessins est sur l'utilité générale de sorte qu'une variété de différentes méthodes pour mesurer la dose soit employable sur le même fantôme. Cependant, les dessins sont en accord raisonnable avec les données anthropométriques rapportées dans la littérature. Les fantômes se sont montrés très utiles aux mesures de dose selon la profondeur et de l'absorption totale d'énergie pour la thérapie par l'irradiation du corps entier. Aussi a-t-on fait des mesures de dose avec la téléthérapie à faisceau, avec des instruments de la brachythérapie et avec des radio-isotopes distribués à l'intérieur du corps.

РАЗДЕЛЕННЫЕ НА СЕГМЕНТЫ МОДЕЛИ НОРМАЛЬНОГО ВЗРОСЛОГО ЧЕЛОВЕКА, ЮНОШИ И РЕБЕНКА

Из имеющихся недорогих материалов была сконструирована разделенная на сегменты модель нормального взрослого человека. Были изготовлены также модели юноши и ребенка. Основным требованием, предъявляемым к модели, является возможность широкого ее применения с учетом различных методов измерения активности. Вместе с тем предлагаемая модель не противоречит опубликованным антропометрическим данным. Модели оказались вполне пригодными для измерения величины дозы и общей энергии поглощения при лечении общим облучением Измерение доз производилось при помощи устройств для теле—и брахйтерапии, а также путем исследования внутреннего распределения изотопов

* From the Medical Division, Oak Ridge Institute of Nuclear Studies, Oak Ridge, Tennessee, under contract with the United States Atomic Energy Commission.

† A more detailed description is available in U.S. Atomic Energy Commission Report ORINS-35.

UNTERTEILBARE PHANTOME VON STANDARDMENSCH, JUGENDLICHEM UND KIND

Ein unterteilbares Phantom des Standardmenschen wurde entworfen und aus leicht erhältlichen und billigen Stoffen gebaut. Ähnliche Phantome wurden auch für den Jugendlichen und das Kind konstruiert. Die grösste Bedeutung wurde dabei der allgemeinen Verwendbarkeit beigemessen, sodass eine Anzahl verschiedener Dosismessmethoden am gleichen Phantom angewendet werden könnte. Die Konstruktionen sind in gutem Einklang mit den aus der Literatur bekannten antropometrischen Daten. Die Phantome erwiesen sich als äusserst nützlich für Tiefendosis- und Total-Energieabsorptions-Messungen bei der Ganz-Körper-Bestrahlungs-Therapie. Dosie-Messungen bei Strahlen-Therapien. Brachytherapie und interner Verteilung von Radioisotopen wurden durchgeführt.

INTRODUCTION

INTERNATIONAL agreement exists on many characteristics of the "standard man".[1] The mass and effective radius of the various body organs in the international standard man have been agreed upon, but no agreement has been reached on the relative mass, volume or effective dimensions of various sections of the body. This information would be required for the design of a compartmentalized phantom for the standard man. MAYNEORD[2] has given the dimensions of a compartmentalized phantom used in a study of integral dose. The reported designs of other phantoms[3,4] have been highly dependent on the phantom studies to be made.

Phantom techniques are in frequent use at the Medical Division. Since little had been reported in the literature on the design of a compartmentalized standard-man phantom, it was thought advisable to construct one of our own design. We felt that the design should be based on reported anthropometric measurements and in addition should provide for use of a variety of measurement techniques. Thus the design was attacked from the viewpoint of maximum utility rather than the immediate requirements of one particular study.

The following characteristics were considered to be desirable in such a phantom: (1) compartmentalization into body segments; (2) reasonable agreement with reported anthropometric measurements; (3) complete accessibility to all parts of the phantom for probe-type measurements and the insertion of mock-ups of organs and bones; (4) simplified geometry to facilitate theoretical treatment, and (5) a minimum cost of construction while still meeting the preceding criteria.

Recent investigations at the Medical Division of the efficacy of treating leukemia with total-body irradiation have led to the design of additional phantoms for a standard adolescent and a standard child. All three phantoms have proved useful in dose studies made here. The following is a description of their design and construction.

DESIGN

Since compartmentalization was a stated requirement, a basic decision on the division of the body had to be made. The simplest way of dividing the human body into sections is by a transverse sectioning perpendicular to the long axis of the body. Also by proper choice of the sites where the sectioning is made, body segments that are roughly uniform in cross-sectional appearance may be obtained. The division decided upon is shown in Fig. 1.

Transverse sections through the human body in most instances resemble either elliptic cylinders or rectangular parallelepipeds.[5] The incidence of each is roughly the same and therefore the choice of either as a basic shape for the individual sections would be equally approximate. Since the

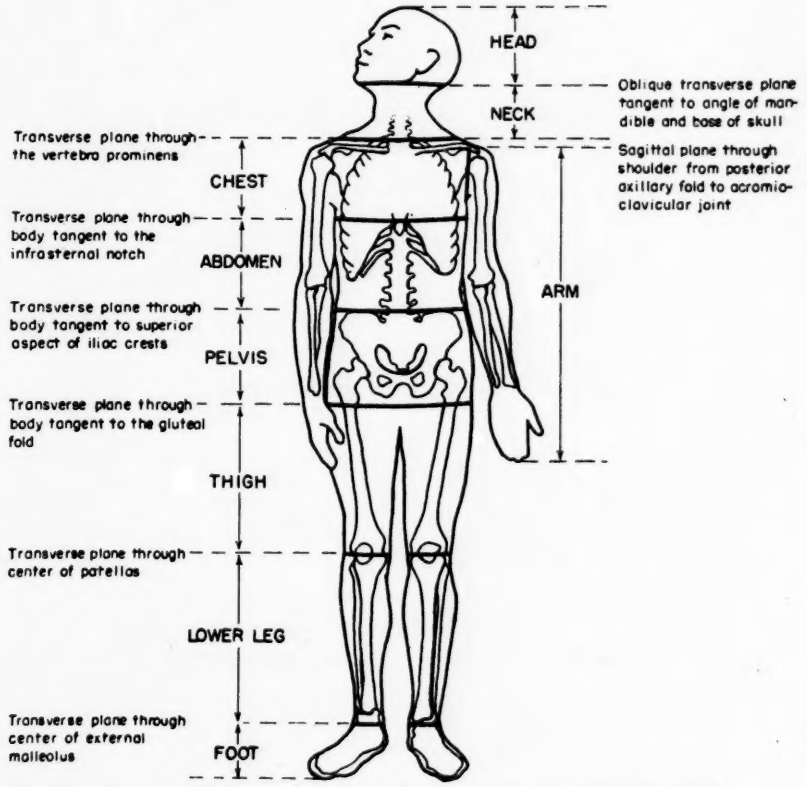
HEAD
NECK
Oblique transverse plane tangent to angle of mandible and base of skull
Transverse plane through the vertebra prominens
Sagittal plane through shoulder from posterior axillary fold to acromioclavicular joint
CHEST
Transverse plane through body tangent to the infrasternal notch
ABDOMEN
ARM
Transverse plane through body tangent to superior aspect of iliac crests
PELVIS
Transverse plane through body tangent to the gluteal fold
THIGH
Transverse plane through center of patellas
LOWER LEG
Transverse plane through center of external malleolus
FOOT

FIG. 1. Body sectioning adopted for design of compartmentalized phantoms.

design criteria called for complete accessibility to all parts of the phantom, a rectangular parallelepiped design was adopted. In addition, we found that the cost involved would be considerably less with parallel walls.

The method used in the actual design for the standard man, adolescent and child involved the adjustment of available anthropometric data for variations introduced by the transverse division and rectangular compartmentalization that had been adopted. In making these adjustments many compromises were required, but direct extrapolation was adhered to wherever possible. A detailed report on the design has been published elsewhere.[6] The main source of anthropometric data used was that compiled by KROGMAN[7].

CONSTRUCTION

The individual phantom compartments were made of $\frac{1}{4}$ in. plexiglass sheets, except for compartment sides that were to be facing each other when the phantom was assembled. One-sixteenth inch sheets were used for such faces. Adjoining compartments are thus separated by $\frac{1}{8}$ in. plastic and this in turn introduces an error of about 2 cm in the over-all height of each assembled phantom. Compartment faces were glued together with ethylene dichloride after milling the edges to ensure a watertight seal.

Fig. 2 shows a diagram of the three phantoms drawn to proportion. The phantoms are constructed for assembly in a supine position with the individual compartments

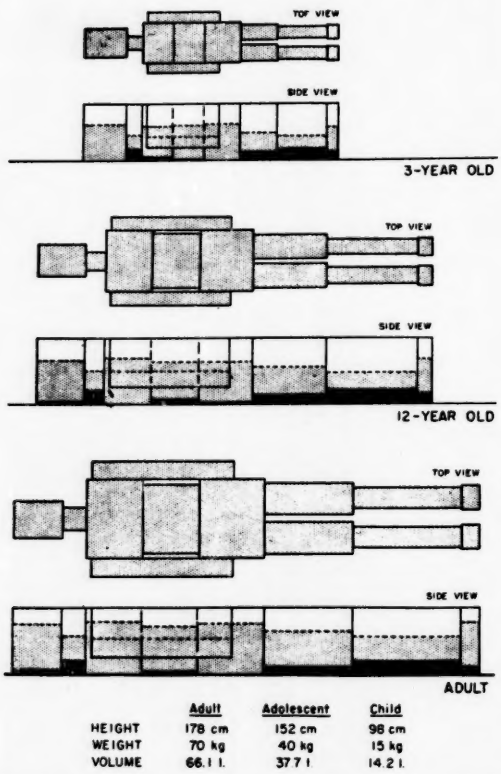

FIG. 2. Diagram showing relative sizes and shapes of adult, adolescent and child phantoms.

supported vertically at various heights so that the assembled phantom will approximate the general contour of the human body. These vertical supports are indicated in black, except for the arm compartments. The over-all height of each compartment is such that the open portions of the compartments will be on a plane with each other when the phantom is assembled. The actual height of the phantom material in each compartment is indicated by a dotted line. Table 1 shows the inside dimensions of the compartments together with the heights of the phantom material and the heights of the compartment supports. Fig. 3 shows a photograph of the three assembled phantoms.

USES

The following examples will illustrate the various types of measurements that have been made or are planned with these compartmentalized phantoms.

Brachytherapy

Radium in a simulated colpostat-tandem was placed in the pelvic sections of the phantoms as a mock-up of radium treatment of carcinoma of the cervix. The dose to the various compartments was determined for a standard 8000 mg-hr treatment.[8] The same procedure has been carried out for other isotopes.

Calibration of linear scanner

The adult phantom was filled with a sodium-24 solution of known concentration to simulate the neutron activation experienced in a total-body irradiation accident.[9]

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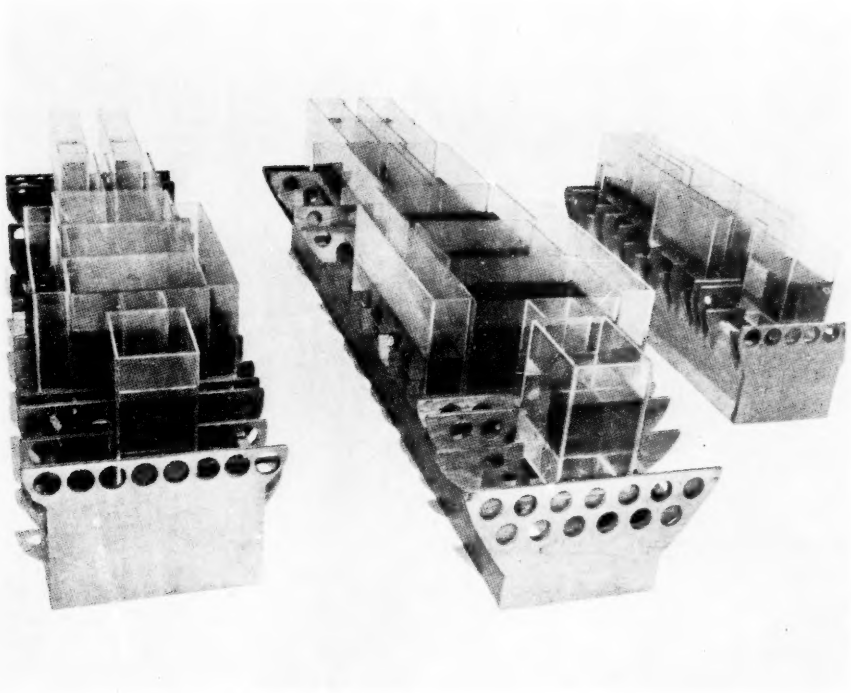

FIG. 3. Photograph of assembled phantoms for adult, adolescent and child.

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TABLE 1. Adult, adolescent and child phantoms

Section	Compartment dimensions (*ID*)			Phantom material height (cm)	Phantom material volume (liter)	Vertical compartment support (cm)
	Length* (head to foot) (cm)	Width* (side to side) (cm)	Height* (front to back) (cm)			
Adult						
Head	19·0	14·0	24·6	17·3	4·60	1·4
Neck	9·0	8·5	20·5	9·1	0·70	5·5
Chest	21·5*	30·3	26·0	20·2	13·10	0·0
Abdomen	21·5	25·9	24·3	16·7	9·30	1·7
Pelvis	25·0	30·3	26·0	18·9	14·30	0·0
Thigh	35·0	11·8	22·6	13·1	10·80 × 2	3·4
Lower leg	40·0	8·0	20·3	8·7	5·60 × 2	5·7
Foot	7·0	9·0	22·3	16·7	2·10 × 2	3·7
Arm	(54·0)	7·0	19·6	7·4	5·60 × 2	6·4
Total	178·0				66·10	
Adolescent						
Head	18·3	12·7	24·4	16·1	3·77	0·6
Neck	7·7	6·8	20·0	7·3	0·38	5·0
Chest	18·0	24·2	25·0	17·3	7·54	0·0
Abdomen	18·0	21·6	23·5	14·4	5·58	1·5
Pelvis	21·0	24·2	24·4	15·3	7·80	0·6
Thigh	28·0	9·6	21·7	10·7	5·73 × 2	3·3
Lower leg	35·0	6·2	19·8	6·9	2·98 × 2	5·2
Foot	6·0	7·1	21·2	13·3	1·13 × 2	3·8
Arm	(46·0)	5·2	18·8	5·9	2·79 × 2	6·2
Total	152·0				37·70	
Child						
Head	16·8	11·5	22·0	14·0	2·70	0·0
Neck	5·7	4·9	17·6	5·2	0·15	4·4
Chest	12·0	16·0	21·0	12·0	2·31	1·0
Abdomen	12·0	16·0	21·4	12·7	2·44	0·6
Pelvis	14·0	16·0	22·0	13·9	3·12	0·0
Thigh	14·0	6·1	18·4	6·8	1·19 × 2	3·6
Lower leg	19·0	4·6	17·6	5·1	0·89 × 2	4·4
Foot	4·5	5·0	18·6	9·5	0·43 × 2	3·4
Arm	(28·0)	4·0	17·2	4·4	0·97 × 2	4·8
Total	98·0				14·20	

* Phantom is assumed to be in supine position.

This phantom was then used to calibrate a linear scanner for use in scanning accident victims.

Integral dose in a total-body γ-irradiation facility

The phantoms were filled with a rad-calibrated chemical dosimeter and placed in the position of a patient in a total-body irradiation device. The integral dose to each of the compartments was then determined by direct measurement.

Isodose lines in a total-body γ-irradiation facility

The phantoms have also been used in a total-body irradiation facility to study point-detector dosimetry. A probe-type detector

was used in aqueous and solid phantom materials to determine isodose lines for total-body irradiation therapy.

Spectrometry in a total-body γ-irradiation facility

Scintillation detectors can be used in the phantoms if low-activity sources are used to mock the therapy sources. The radiation spectrum can be measured directly inside the filled phantom to approximate the spectrum inside the body of a patient undergoing therapy.

Organ specific doses

Hollow plastic organs can be filled with radioactive materials of known concentration and placed in position in the phantoms. The absorbed radiation dose can be determined both inside the body and inside the organs.

SUMMARY OF USES

None of these examples involves a determination of absolute dose; however, each approaches a situation that can be matched in the human patient. They all have the advantage of being measurements, but they have the added advantage of being susceptible to theoretical calculations. These standard child, adolescent and adult phantoms are adaptable to a wide range of useful measurements. Although we feel that our stated objectives have been achieved, we do not wish to imply that these phantoms supplant others that have been described. Rather they represent an addition to a well-known methodology.

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Stereoautoradiography

(*Received* 9 *November* 1959)

THE photographic emulsion is the type of detector best suited for studies of the two-dimensional distribution of a radioactive material. Thus the autoradiographic technique has been used with great success for many different types of such studies, as is well known.

In certain cases, however, other detectors must be used and as an example may be mentioned studies of a radioactive tracer in the human body by means of a scintillation detector giving a "scintigram".

By combination of two detectors measuring in cross-directions—i.e. giving scintigrams in two perpendicular planes—it is also, as is known, possible to get a picture of the spatial distribution of the tracer.

It should, however, be possible to get a more detailed three-dimensional picture of the spatial distribution by means of a photographic emulsion.

Technique

The pin-hole camera has been used *inter alia* for studies of strong radioactive sources.[1] For three-dimensional studies we have constructed a pin-hole camera with three pin holes (*two* pin holes are sufficient, Fig. 1).

The mask is thick enough to absorb the β-rays from the specimens and the diameter of the holes (approx. 1 mm) large enough—as compared with the thickness of the absorber—to allow the radiation from all specimens to reach the photographic emulsion. (It should be noted that the cylindrical holes used in the present design of the camera give a somewhat poorer resolution than an arrangement with double-conical holes.)

In one experiment three neutron-irradiated tungsten wires, with an activity of approximately 1 mc each (W^{187}, 24 hr half-life, 70% 0·63 MeV β^-, several gammas) were placed on a staircase with 10 mm distance between the planes. After 1 hr exposure in vacuum the film (Ilford G) was developed, giving a picture as shown in Fig. 2. It is clearly seen from the figure that it is possible to calculate the spatial positions of the different specimens from the distances between the different autoradiographs of each specimen. The results of these calculations are given in Table 1.

Conclusions

It has been found possible to use a stereo pin-hole camera for studies of the spatial distribution of a radioactive material. The camera has been used for β-emitting nuclides but it should be possible to adopt it also for γ- and α-emitters. It should be pointed out that the present technique can be much refined and that, eventually, scintillation detectors or others might be used in order to reach applications of obvious value, e.g. spatial activity distribution studies on living men or animals or maybe trees. Moreover, it should be possible, as suggested by HALLERT[2], to use common stereophotogrammetric methods and instruments for studies and precise measurements in three dimensions of stereoautoradiographs. See for instance Reference [3], concerning the basic principles of such measurements and an outline of the theory of errors. A more detailed study of the theory of errors and methods for the

TABLE 1. (cf. Fig. 2)

$h = 10$ mm $\quad z_2 = 19{\cdot}5$ mm $\quad x_1 = 0$ (d assumed to be $= 0$)

	z_1		z		x_2	
	Calculated	Known	Calculated	Known	Calculated	Known
Sources *AB*	40	42	8	10	11	11
Sources *BC*	30	32	10	10	15	15

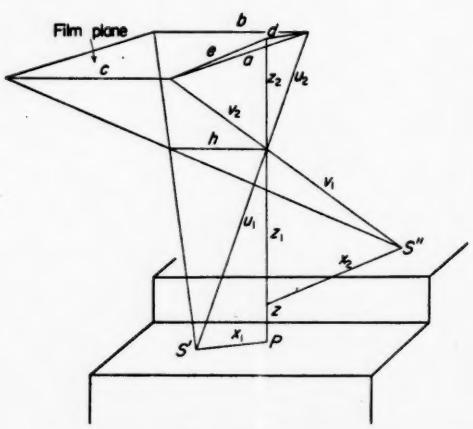

FIG. 1. Stereo pin-hole camera with two pin holes.
h is the distance between the pin holes
z_2 is the distance between the film plane and the pin-hole plane
z_1 is the distance between the pin-hole plane and the plane of source S''
z is the distance between the planes of the sources S'' and S'
x_1 and x_2 are the planar "co-ordinate" for the sources S' and S'' from P.

The following equations are readily deduced.

$$\frac{z_1 + z_2}{z_1} = \frac{v_1 + v_2}{v_2} = \frac{c}{h}$$

$$\frac{z_1 + z}{z_2} = \frac{u_1}{u_2} = \frac{h}{b - h}$$

$$\frac{x_1}{d} = \frac{z_1 + z}{z_2} = \frac{h}{b - h}$$

and thus

$$z_1 = \frac{z_2 h}{c - h}$$

$$z = -z_1 + \frac{z_2 h}{b - h}$$

$$x_1 = \frac{dh}{b - h}$$

$$x_2 = \frac{eh}{c - h}.$$

S' and S'' are the radioactive sources.
P is the vertical projection of the "right" pin hole n the lower source plane.
The line connecting S' and P is parallel to the corresponding line in the film plane.
Thus the vertical and horizontal distances between S' and P are obtained as well as the direction $S' - P$, i.e. the position of S' is unambiguously determined. In analogy with this the position of S'' and other sources can be obtained.

Continued from previous page]

determination of the accuracy of the photogrammetric procedures is made in Reference [4].

Acknowledgements—Thanks are due to O. LAMM, Professor of Physical Chemistry, for his interest in this work and to B. HALLERT, Professor of Photogrammetry, for inciting us to endeavour in this field and for a valuable discussion on stereophotography.

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A Three-channel Low-background Counting Unit

(*Received* 17 *May* 1960)

LOW-BACKGROUND counters based on anti-coincidence circuits are in general use for the assay of low-activity β-emitting samples.[1,2] The unit to be described was designed and built in the Regional Physics Department for measurements in the range 1–10 counts/min on Sr^{90} and Y^{90} samples. It has the following features: (a) three channel operation without interaction, (b) continuous operation without adjustment of controls, and (c) ease of sample presentation.

Construction of castle

As shown in Fig. 1, three end window GM4LB counters are mounted on a brass framework at the centre of a cylinder formed by the screen Geiger tubes, type G.26Pb. Sixteen of these tubes, each 11 in. long, are arranged in a double layer to form the surface of the cylinder and each end is closed by a vertical bank of five counters. The complete assembly is contained in a 4 in. thick shield built from steel bricks. The external dimensions are 30 × 20 × 24 in. high and the total weight is $1\frac{1}{2}$ tons. The samples, which are prepared on standard metal disks, are held in brass slides which are then inserted through small slits in the castle. The outputs of the end

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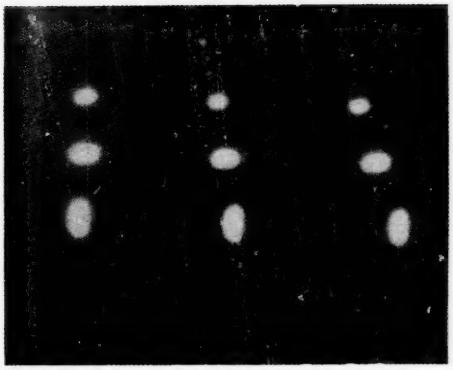

FIG. 2. Stereoautoradiograph obtained in a camera with three pin holes (×2).
Source *B* symmetrically arranged over the point *P* in Fig. 1.
[See article by ERWALL and WESTERMARK]

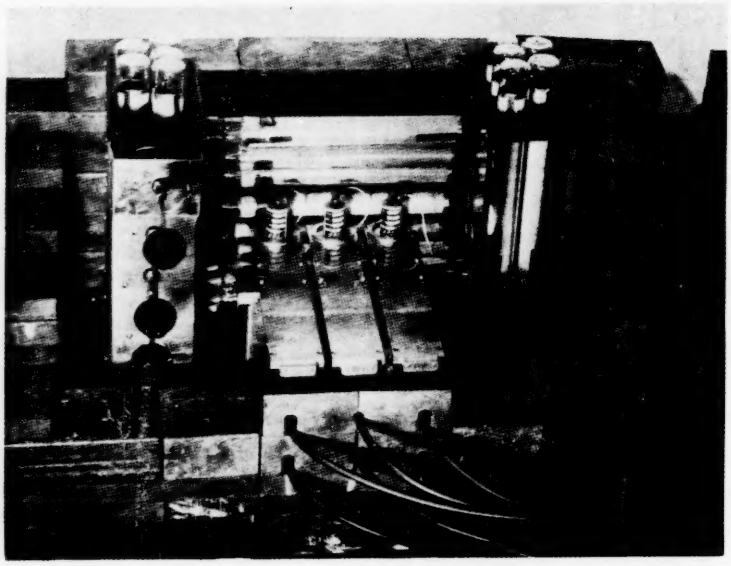

FIG. 1. Counting and screening assembly.

window counters are fed into three pre-amplifiers located in the castle. The combined outputs of the screen tubes are applied to another pre-amplifier. By a suitable switching arrangement monitoring of individual screen tubes is provided. Since the apparatus is limited to pure β-emitters there is no interaction between channels when samples are counted simultaneously.

Electronic counting equipment

This consists of three identical channels. Each channel comprises the following:

(a) *Stabilized power supply.*

(b) *Anti-coincidence unit.* This incorporates twin pulse amplifiers, pulse shapers, variable delay circuits, and anti-coincidence circuit.

(c) *Discriminator and counting unit.* The sample count rates are in the range which can be counted directly by a mechanical register. The complete counting unit consists of a voltage-discriminating amplifier, a pulse lengthener and a driver stage for a mechanical register.

R.F. oscillator E.H.T. supplies

Four are required. These give outputs continuously variable in the range 0–2000 V. The voltages are monitored by meters mounted on the front panels. The use of stabilized H.T. supplies in conjunction with R.F. oscillators ensures high E.H.T. stability.

Shielding and screening efficiency

Table 1 shows the background count-rates at various stages of castle construction, with and without screening.

The GM4LB input sockets to each anti-coincidence unit are duplicated to enable the unscreened background to be monitored simultaneously with the screened background. This simplifies the setting-up procedure.

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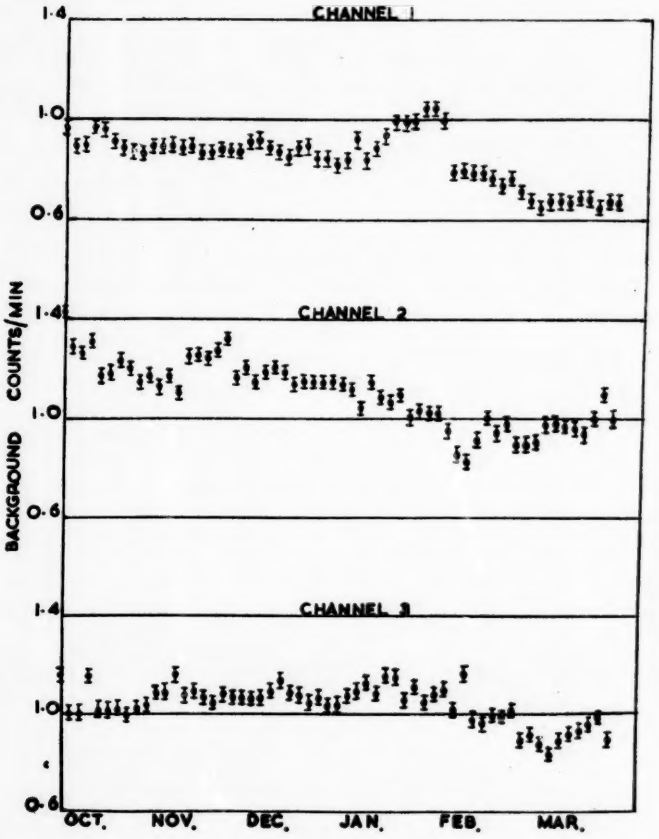

FIG. 2. Record of background variations.

TABLE 1

Shielding	Unscreened (counts/min)	Screened (counts/min)
Base	12	6
Base + walls	8	2·5
Base + walls + roof	6·5	1

Counting procedure

After initial setting-up no further adjustment of controls is necessary. The counting procedure merely consists of the insertion of samples and the operation of count switches. The changing of samples is quickly and simply carried out. Each sample is counted for 24 hr, the background being taken as the mean of the count-rates for the 24 hr before and after the sample count. Fig. 2 shows the variation of the background count-rate for each channel from October 1959 to March 1960. The proper functioning of the unit is checked each day by monitoring the background for 2 hr. This is incorporated in the above counting sequence.

Counting efficiency

The counting efficiency for strontium-90 was estimated by using a standard sample of 0·01 mμc. The percentage efficiency for each channel has remained within the limits of 33·0–34·1, 40·7–42·5, 33·4–34·6, respectively. The efficiency for yttrium-90 was about 20 per cent using a standard of 0·02 mμc.

Conclusions

The unit described has been in continuous use for 6 months during which time approximately 100 samples of low-activity Sr^{90} have been assayed. The operation of the unit has been so simplified that these assays are now part of the routine duties of the laboratory assistants.

Acknowledgements—The authors would like to thank Dr. J. M. VALENTINE for his help and advice and to acknowledge a grant of money from the Medical Research Council for the purchase of components.

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A Simple Plastic Scintillation Counter for Tritiated Hydrogen

(*First received* 28 *April* 1960
and in final form 12 *May* 1960)

THIS detector was designed to measure the tritium content of hydrogen coming from a palladium chromatography column.

The requirements were for a sensitive detector with a small, vacuum-tight volume. The method of construction is illustrated in Fig. 1. A rectangular piece of plastic phosphor* 0·1 mm thick was heated in a stream of hot air, bent into a cylindrical shape, and inserted in the 5 mm bore Pyrex tubing with short lengths of coiled wire at either end to retain it in position. The glass was passed through a diametrical hole in a cyclindrical perspex light guide to which it was optically coupled with silicone oil. The sides and end of the light guide were coated with a diffuse reflector of antimony dioxide-based paint.

* Type NE 102 Nuclear Enterprises Ltd., Edinburgh.

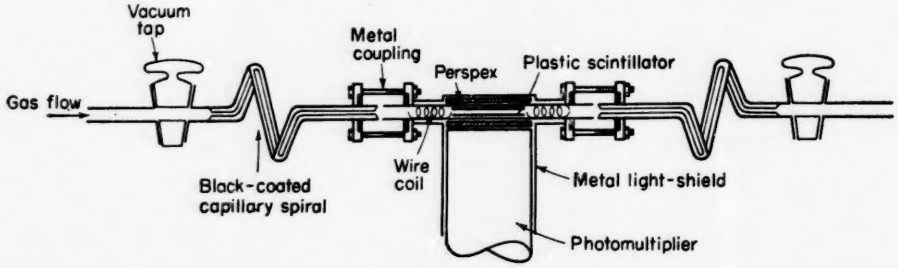

FIG. 1.

A single spiral of capillary tubing joined on to each end of the detector by means of metal couplings combined with a coating of black paint over the whole assembly, was sufficient to exclude extraneous light. The photomultiplier* used had a dark current of 0·006 μA (better photomultipliers are now available). The sensitive volume of the detector was 0·5 ml and when filled with tritiated hydrogen to a pressure of 66 cm of mercury, an efficiency of 2·2 per cent was obtained with a background of 5 c/s at room temperature of 20°C.

The initial background on assembly was considerably higher, due to the phosphorescence of the antimony dioxide paint, but decayed to the level quoted in two days.

There is undoubtably considerable loss of light along the glass tubing and the use of a cylindrical glass or perspex cell with circular pieces of plastic phosphor on the ends would probably lead to a considerable increase in performance.

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Wantage Research Laboratory J. F. Cameron
(*A.E.R.E.*) K. J. Taylor
Wantage

* Type 9524B EMI Electronics Ltd., Hayes, Middlesex.

A High Intensity Cesium-137 Research Irradiator

(*Received* 9 *May* 1960)

The design, installation and calibration of a 12,000 c Cs^{137} research irradiator of the Notre Dame type has been completed at the Georgia Institute of Technology. Fabrication of the source was sponsored by the Office of Isotopes Development, U.S. Atomic Energy Commission, under contract AT (38-1)-202. The dose rates are 1.4×10^6 rad/hr in the center sample hole and 1×10^6 rad/hr in the outer sample holes.

The Notre Dame tube nest[1] consists (Fig. 1) of a circular array of brass tubes such that a source of the active material can be positioned at each 30° interval around the center point. The Georgia Tech. irradiator has twelve sources (approximately 1000 c each) of Cs^{137}, in the form of CsCl, of specific activity in the range of 17–21 c/g. The sources are $\frac{1}{2}$ in. in diameter by 12 in. in length (active material length of 6 in.).

Approximately 150 g of material with a bulk density of one can be lowered into the center sample hole where it will be exposed to a homogeneous

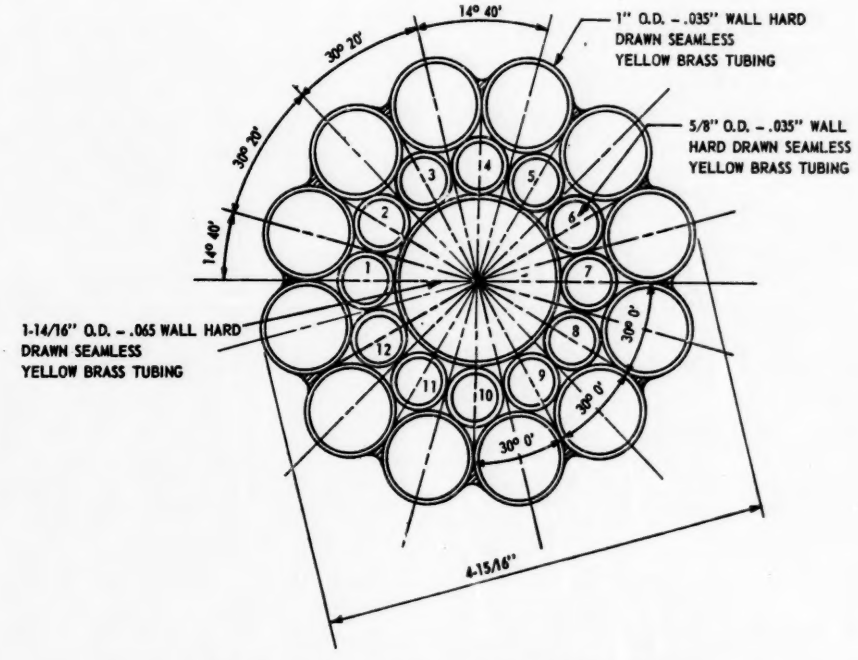

Fig. 1. Horizontal cross-section of the tube nest.

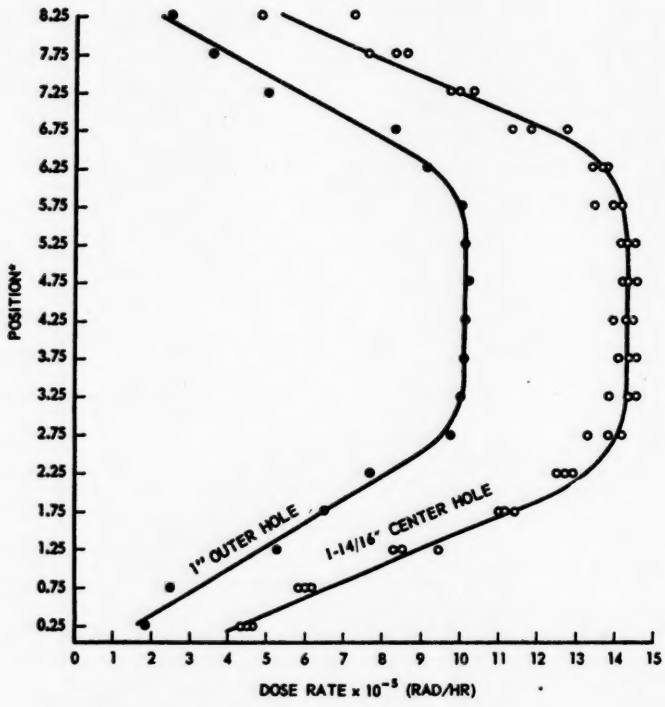

FIG. 2. Dose variance with vertical movement.

radiation field of 1.4×10^6 rad/hr. Approximately 40 g with a bulk density of one can be exposed in any one of the twelve outer holes to a homogeneous radiation field of 1×10^6 rad/hr. Fig. 2 is a plot of dose variance with vertical movement through the irradiation area and is an indication of the homogeneity of the radiation fields.

Dosimetry measurements were performed with Du Pont MSC-300 cellophane[2] which was calibrated with the ferrous ion oxidation system. The cellophane samples were placed at various locations in the source for total doses ranging from 1×10^6 to 30×10^6 rad. The absorbance change in the cellophane was detected by a Beckman Model-B spectrophotometer.

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A New Production Process for Tellurium-132

(*Received* 23 *May* 1960)

Introduction

IN the production process for the separation of tellurium-132 from irradiated uranium and other fission products[1], uranium metal, usually in the form of wire, is dissolved in nitric acid. This is inconvenient as it is the slowest single stage and the nitrate ion must be removed as its presence interferes with the subsequent precipitation of tellurium metal.[1] Alternatives to the use of metal, such as oxide pellets[2] were found to offer no advantage. The metal however does dissolve rapidly in hydrochloric acid. When tried with irradiated uranium, the yields of Te^{132} with added carrier were much lower than expected, in some cases only 10 per cent. It was found that a black stain, highly γ-active, formed in an absorption tube containing "Sofnolite" used to treat the gases evolved on dissolution, and

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that the losses were due to the formation of hydrogen telluride. This was removed from solution with the gas formed on dissolving the uranium and partially decomposed to leave a black deposit of tellurium in the tube. The known formation of H_2Te by the action of a non-oxidizing acid on a metallic telluride[3] accounts for the production of volatile tellurium compounds, since the formation of uranium telluride is clearly possible, but the usual action of metals on tellurous acid (the carrier used) in acidic solution is to produce the element. The rapid formation and high yield of H_2Te from H_2TeO_3 was therefore surprising. It was possible that the reducing agent was uranium tri- and/or tetra-chloride, produced when uranium metal dissolves in hydrochloric acid. This is analogous to the action of titanium trichloride which forms H_2Te from tellurous acid in acetic acid solution.[4] However, experiment showed that this was not so and reduction to H_2Te took place only in the presence of dissolving uranium.

The reaction appeared to offer a rapid and simple separation of Te^{132} from most fission products, and this promise was confirmed by experiment.

Preparation of hydrogen telluride

Preliminary experiments with inactive materials confirmed that tellurous acid and also tellurium metal were readily reduced to H_2Te by the uranium–hydrochloric acid system. It was also apparent that the reduction must be carried out in an oxygen-free atmosphere because of the ease with which H_2Te is oxidized. This was only partly supplied by the hydrogen from the reaction of uranium with hydrochloric acid, so a slow current of gas was passed through the reacting mixture to maintain the inert atmosphere and to sweep out the hydrogen telluride before it decomposed. This was very necessary towards the end of the reaction when the evolution of hydrogen was slow. Nitrogen, hydrogen and helium were suitable carrier gases, but if xenon-133, also produced in fission, was to be separated, hydrogen or helium were used, because nitrogen interfered with the absorption of xenon on charcoal at $-50°C$, after the H_2Te had been removed. Hydrogen did not appear to assist the reduction to hydrogen telluride.

During the dissolution, hydrochloric acid ($\sim$6 M) was added continuously to control the reaction, as it became undesirably vigorous if the total quantity of acid was added initially. The tellurium carrier (as tellurous acid) was added in the hydrochloric acid to maintain a continuous supply of carrier because the H_2Te was formed and given off rapidly. A total of about 70 mg of tellurium was normally used, but separation was effective with smaller amounts (e.g. 20 mg). Although the apparatus was thoroughly washed with water prior to use, tellurium metal was deposited at the beginning of the reaction wherever the apparatus had been cleaned with an oxidizing agent. However, as the reaction proceeded the solution became hot and there was some refluxing which washed most of the deposited tellurium back into the solution, when it was again reduced.

The reaction of irradiated uranium with hydrochloric acid in the absence of carrier, evolved carrier-free Te^{132}, but yields were low (about 10%) probably because of decomposition of hydrogen telluride on to the walls of the reaction vessel.

The uranium and hydrochloric acid mixture reduce other elements to volatile hydrides, e.g. arsine, stibine and hydrogen selenide. Fortunately the irradiation time of 1 week for a good yield of Te^{132} and the low fission yields of possible contaminants allowed Te^{132} to be separated with high radiochemical purity. A search made for Sb^{127} in the final product indicated that the amount was less than 0·01 per cent. There was a very small contamination with iodine isotopes also produced in fission. It was likely that all the iodine was present in the reduced state with little possibility of oxidation to iodine. The partial pressure of hydriodic acid is too low even at 100°C for significant contamination of the separated Te^{132}. The amounts of impurities were further reduced in purification steps subsequent to the separation of the H_2Te.

Absorption of hydrogen telluride

The gaseous H_2Te must be absorbed by a suitable solution for further treatment. An alternative was to condense it, but this was inconvenient when handling several hundred millicuries of activity.

Various solutions were tried as absorbents. Absorption by alkaline hydroxide solution was inefficient with or without the presence of hydrogen peroxide. With dilute ammonia, absorption was rapid and usually the solution turned purple. When exposed to the air a layer of tellurium metal formed on the surface of the liquid, which redissolved on shaking until the point was reached when all the tellurium would precipitate. In some cases a finely divided precipitate of tellurium metal was produced and absorption was inefficient.

It is known that ferric chloride oxidizes hydrogen telluride to tellurium[5] which also dissolves in ferric chloride solutions to give tellurous acid.[6] When hydrogen telluride was passed into a solution of ferric chloride in 3 M HCl, the bubbles of gas blackened and then became clear. The absorption was found to be complete and tellurium could be precipitated readily by reducing agents, e.g. stannous chloride solution.

Production process

Uranium wire, irradiated for a suitable period[1], was transferred to the dissolving vessel of the apparatus illustrated in Fig. 1. An inert atmosphere of nitrogen or helium was maintained in the apparatus during the reaction, and the reaction proceeded as already described. The gases from the dissolver were passed into a solution of 5% ferric chloride in ~3 M hydrochloric acid. Metallic tellurium was precipitated from this solution by the addition of stannous chloride solution in excess of the amount for the reduction of the ferric to ferrous state.

The radiochemical purity of the filtered tellurium precipitate was sufficiently high to require no further treatment other than washing with ~5 M hydrochloric acid and water. If for any reason (e.g. splashing from the reducing solution) another purification was necessary, the washed tellurium precipitate was dissolved in the minimum quantity of strong nitric acid, and tellurium reprecipitated by stannous chloride from a solution of hydrochloric acid and hydroxylamine hydrochloride. The washed tellurium precipitate was then converted to the chemical form required. The demand was usually for a solution of Te^{132} as sodium tellurite, which was produced by dissolving the precipitated tellurium metal in a minimum of strong nitric acid, adding 5% sodium hydroxide solution until the precipitate of tellurium dioxide which was formed just redissolved, and adjusting the pH of the solution with dilute hydrochloric acid to between pH 8·5–9·0.

The overall yield of Te^{132} produced as sodium tellurite solution was over 90 per cent. The efficiencies of separation and absorption of Te^{132} as hydrogen telluride were each over 95 per cent.

Apparatus

The apparatus used for tellurium-132 production is shown diagrammatically in Fig. 1. This is routinely used to separate quantities of Te^{132} of the order of 200 mc per week. It comprises a dissolving flask with remotely operated facilities for the addition of reagents, stirring and removal of effluent and an absorber vessel which is a modified form of the reaction vessel described by Stang and Levy.[7]

The tendency for hydrogen telluride to decompose, necessitates a short uninterrupted path from the reducing to the absorbing solution. Without a spray trap the separated Te^{132} contains about 15 per cent of γ-emitting impurities, but a baffle in the neck of the flask reduces contamination to ~1 per cent. Most of the impurities are removed from the precipitated tellurium metal by washing with hydrochloric acid.

The design of the spray is important as it allows any tellurium metal deposited to be washed back into the reducing solution. A glass wool filter for example soon becomes choked with tellurium metal which would not be returned to the flask.

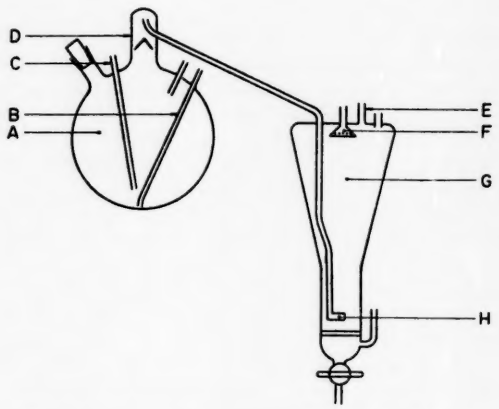

Fig. 1. Apparatus for separation of hydrogen telluride. (A) 500 ml dissolving flask, (B) effluent removal line, (C) gas inlet, (D) spray trap, (E) gas outlet, (F) water washing spray, (G) 250 ml absorber vessel, (H) gas bubbler.

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The Incorporation of Iodine-132 into Organic Compounds

(*Received* 16 *May* 1960)

Introduction

Many organic compounds are difficult or impossible to synthesize with radioactive components but often

they will react with radioactive iodine to form an iodinated compound. The objection to this approach is the difference in physical and chemical properties between the iodinated and the original compound. These differences, however, may be unimportant or sufficiently small for many useful experiments and, for example, iodinated human serum albumin has established clinical uses.

Iodine is usually introduced into a compound by reaction with a solution of iodine[1] or of iodine chloride.[2] A technique applicable to "carrier free" iodine isotopes has also been described[3] in which a suspension of an aqueous solution of iodide in an unsaturated oil or wax is heated at a temperature above the boiling point of water for about 4 hr, during which time all the water is removed and the organic material reacts with the iodine. Clearly the length of the heating period is too long for iodine-132 and the boiling points of the oils or waxes should preferably be much higher than that of water.

The principal radioactive iodine isotopes are those of mass 131, half-life 8·05 days and those of mass 132, half-life 2·33 hr. Iodine-132 is available from the decay of tellurium-132, a fission product of uranium, which decays thus:

$$Te^{132} \xrightarrow[t_{1/2} = 77\text{ hr}]{} I^{132} \xrightarrow[t_{1/2} = 2{\cdot}33\text{ hr}]{} Xe^{132}\ (\text{Stable}).$$

As the half-life of I^{132} is relatively short, it may be used to advantage for some tracer experiments, particularly industrial ones where the rapid decay ensures that there will be virtually no residual radioactivity by the day following the experiment. The disadvantage is the necessity to separate the I^{132} from the Te^{132} with which it is in equilibrium as near to the time of use as possible for the maximum amount of I^{132} to be available.

Sources of I^{132} and their preparation

Iodine-132 in equilibrium with Te^{132} is produced at A.E.R.E., Harwell, as a solution of sodium tellurite or as an I^{132} generator[4] which contains Te^{132} absorbed on a column of chromatographic grade aluminium oxide from which a solution of I^{132} as iodide is easily prepared by washing the column.

In the first case the sodium tellurite solution containing Te^{132} is acidified to about 2–3 M and a little hydrogen peroxide (100 vol) is added. To saturate any "reactive impurities" which might form stable iodine compounds, about 2 mg of iodine carrier is added and an air current is passed through the solution for 1–2 hr. The iodine separated is absorbed in alkaline solution. After allowing sufficient time for the re-growth of I^{132}, it may be separated further in the carrier-free state as required. If carrier iodine is necessary, it should be added with a little hydrogen peroxide before each I^{132} separation.

In the second case, the solution of I^{132}, separated from the I^{132} generator in approximately M/100 NH_3 solution, is acidified to about 3 M with concentrated sulphuric acid and a small amount of hydrogen peroxide added. The I^{132} can be separated immediately by passing an air current for 20–30 min. Yields of iodine separated have been about 50 per cent. It is also necessary to pre-iodinate the sulphuric acid to saturate reactive impurities and to distil off the excess of iodine. The time to remove iodine-132 from this solution is reduced by the heating resulting from the addition of concentrated sulphuric acid.

Labelling techniques

Method A. Where laboratory facilities are available, a modification of one of the techniques[3] described above is suitable for I^{132} separated from an I^{132} generator. The compound to be labelled must be unsaturated and experiments have been made only with compounds with boiling points above that of water. A solution of I^{132} as iodide from the generator (about 20 ml of M/100 NH_3 solution) is thoroughly mixed by stirring or shaking with the oil or wax; some heating may be necessary to melt the wax or lower the viscosity of an oil. The mixture is heated in an oil bath at a temperature above the boiling point of water and a rapid current of air passed through. Usually the water will be completely removed and the oil or wax permanently labelled within 1 hr. As this process corresponds to steam distillation some oil or wax, the amount depending on its boiling point, will be removed with the steam and some I^{132} will be associated with this. The amounts of oils or wax lost are small when compounds of high boiling points are used.

The yield of I^{132} from the generator is approximately 60 per cent and there is decay during the labelling process, so the overall yield of I^{132} in the labelled compound cannot be high. Nevertheless, the I^{132} is handled only in solution so the hazard and consequences of an accidental spill are small.

Method B. A method which can be applied to most unsaturated oils and waxes, and with varying degrees of success to saturated compounds makes use of the passage of a gas through a solution containing I^{132} as molecular iodine. The iodine is carried by the air current which is led into the compound to be labelled. Suitable traps remove spray and dry the air current where required.

If the I^{132} generated from a solution is in equilibrium with Te^{132} it is necessary to pass air through the solution for about 1 hr at room temperature for a

TABLE 1

Compound	Method of iodination	Remarks
Olive oil	A	Permanently labelled, oil slightly discoloured.
	B	Permanently labelled
Linseed oil	A, B	Permanently labelled
Lard oil (B.P. Ltd.)	A, B	Permanently labelled
Castor oil	A	Permanently labelled, oil discoloured.
	B	Permanently labelled, warming assists passage of air current
n-Hexane	B	10–20 per cent I^{132} could not be removed. Cooling is necessary during passage of air current to reduce evaporation
Oil—Shell Spirax 140	A	Permanently labelled.
	B	Permanently labelled. Oil requires warming for passage of air current
Paraffin oil (kerosene)	B	Permanently labelled
Petrol M/T fuel grade III	B	Permanently labelled. Cooling is necessary to reduce loss by evaporation
Lubricating oil M. 160	A	Permanently labelled.
	B	Permanently labelled. Warming assists passage of air current
Teepol	B	60 per cent of I^{132} could not be extracted from teepol. Not recommended because of foaming
Detergent DEEPIO (Thomas Hedley & Co. Ltd.)	B	10–15 per cent of I^{132} could not be removed from detergent particles by benzene or carbon tetrachloride even after treating solution with acid and peroxide. Uniformly labelled particles are difficult to obtain and vigorous stirring would be required during passage of air current
Human serum albumin	B	Not recommended because of extensive foaming

maximum yield of I^{132} in the labelled compound. If the I^{132} solution can be heated to just below boiling the labelling time is reduced to about 5 min. In practice, the iodine may be passed into the compound until it is required for use, as the iodine in the iodinated compound will be in radioactive equilibrium with the Te^{132}. This method has the disadvantage of deliberately volatilizing the iodine, but the overall yields are higher than by method *A* and no services are required other than a supply of compressed air. No handling of a liquid source is necessary after the solution of Te^{132} has been loaded into a generator of the type illustrated in Fig. 1. Suitable shielding could be devised to make this easily portable.

Iodine-132 solution separated from an I^{132} generator may be used but yields have been lower and less reliable. As there is radioactive decay during the iodination, the separated I^{132} must be used immediately and the duration of passage of the air current should be reduced to 20–30 min. The apparatus also requires to be recharged with separated I^{132} solution before use.

Most oils may be labelled by this method. The more volatile liquids require cooling to reduce evaporation and the heavier viscous oils require heating to reduce viscosity. This is essential for efficient contacting of the air current with the heavier oils.

Results

Permanent labelling was considered to have taken place when the I^{132} could not be separated from an oil

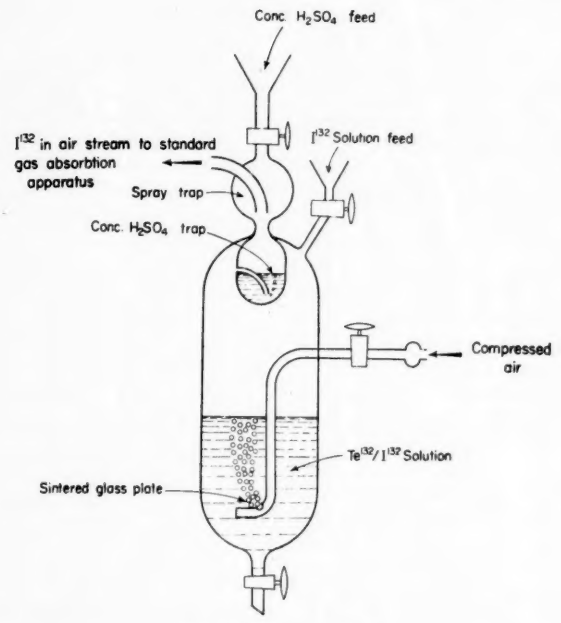

FIG. 1. I^{132} generator.

by treatment with sodium bisulphite solution and sodium thiosulphate solution after making allowance for any solubility of the oil in these solutions. Labelling of a water soluble compound was considered permanent when the iodine could not be extracted into benzene or carbon tetrachloride after acidification and the addition of a little hydrogen peroxide.

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The Preparation of Krypton-85—Clathrate Compounds

(*Received* 29 *February* 1960)

CHLECK and ZIEGLER[1] have described their method of preparing clathrate compounds containing krypton-85 and proved that the compounds remain stable under specified conditions. In 1957, we prepared similar clathrates, but adopted the standard technique evolved by POWELL[2] whereby a saturated solution of quinol containing a small excess of quinol crystals was subjected to a high pressure of Kr, the solution then heated to dissolve the excess quinol, and slowly cooled to form the clathrate crystals. Using a pressure of 20 atm and cooling slowly from 95°C to ambient temperatures in 72 hr, POWELL achieved 75 per cent occupancy of the available cavities.[12] In our procedure, with a similar pressure but heating only to 55°C and cooling in about 2 hr, we achieved 80–90 per cent occupancy.[3] This, however, necessitated rapid stirring of the solution, and the use of a solution consisting of 25 per cent ethanol and 75 per cent water. The alcohol served the dual purpose of increasing the solubility of Kr in the solution, thus increasing the trapping efficiency of the clathrate, and also preventing undesirable frothing

when the solution was degassed. Even at a pressure of only 8 atm and cooling time of ¾ hr, we achieved 60–70 per cent occupancy.

Two preparations, employing about 0·2 per cent Kr-85 in krypton, were stored in stoppered bottles containing undried laboratory air. We found the Kr content per unit weight of clathrate dropped appreciably during the first 3–4 months. The loss during the first month amounted to about 10 per cent of the enclosed Kr, and during the subsequent 2 months another 5–10 per cent loss was recorded. No subsequent analysis of the active clathrate was recorded for a further 28 months, when it was discovered no further measurable loss of Kr had occurred, but that about 3 cm^3/g of an H_2, CO, CO_2, CH_4 mixture was evolved with the Kr on destructive analysis. An inactive sample under similar conditions remained stable. We attribute the initial loss of Kr and the formation of the other gases to the effect of beta radiation on quinol in the presence of moist air. This is supported by the change in colour of the crystals from colourless to dark brown, the dark colour being retained when the crystals are melted. It is possible that a protective layer of solid decomposition products is gradually formed on the surface of the crystals, and the rate of gas evolution is accordingly reduced.

The stability of the Kr-85 clathrates prepared by CHLECK and ZIEGLER can perhaps be attributed to the maintenance of the active clathrates in a very dry state.

We were at the time only interested in producing a solid Kr-85 source which could be used to energize phosphors for the manufacture of light sources, and accordingly we required a compound which was stable under normal atmospheric conditions. Using the mixture with phosphor applied to a surface as a paint, we found the decay in light intensity was comparable to the loss of Kr-85 over the period tested. An attempt to stabilize the compounds by incorporating them into a plastic matrix was only partly successful.

A more detailed account of our work will appear later.

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Gamma Irradiation of Some Unsaturated Steroids

(*Received* 15 *January* 1960)

INFORMATION on the effects of ionizing radiation on steroids is limited and confined mainly to solutions in water and organic solvents.[1] In view of the potential

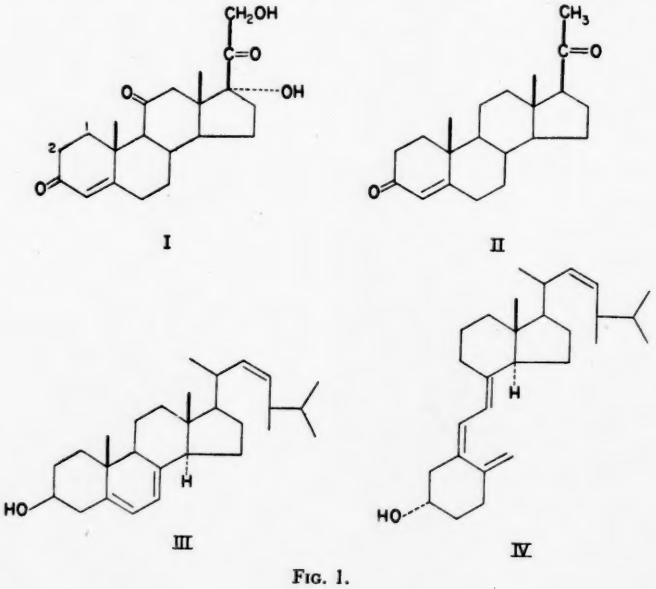

FIG. 1.

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application[2,3] of γ-radiation (Co^{60}) to the sterilization of steroids and other pharmaceuticals and the frequent instability of C^{14}-labelled compounds (e.g. cholesterol-4-C^{14}) to self-decomposition in the presence of oxygen,[4] further knowledge of radiation effects on biologically important steroids appeared desirable. Attention has been focussed mainly on powdered samples.

The steroid hormones, cortisone(I), prednisone (I with 1 : 2-double bond) and progesterone(II) show high stability to radiation damage at super-sterilization doses (e.g. 6–18 Mrad) both in the presence and absence of air. After a dose of 18 Mrad (in air) these hormones showed only small changes (less than 3 per cent) in melting point (decrease), optical rotation and ultra-violet light absorption coefficient (at the maximum). Infra-red spectra showed no detectable changes whilst paper chromatography revealed only the parent steroids. In spite of these criteria, progesterone developed a yellow colour and resinous odour at the higher dose levels. Subsequent crystallization afforded the pure steroid in high yield.

Ergosterol(III) and calciferol (5:6-cis-vitamin D_2) (IV) are sensitive to radiation-induced oxidation in air. In the absence of oxygen these compounds are relatively stable to radiation. At least six irradiation products are formed from ergosterol (paper strip analysis) in ca. 15 per cent total yield after a dose of 18 Mrad. No pure compounds could be isolated but the products appear to contain more oxygen functions than ergosterol.

Irradiation of calciferol in air affords a peroxide and other non-peroxidic substances. The latter may be related to the toxisterols which have been obtained by ultra-violet irradiation of ergosterol (in ethanol).[5] During γ-irradiation the light absorption of the vitamin moves to shorter wavelengths as previously observed with ultra-violet radiation (in benzene)[6] and with X-rays.[7]

Peroxide formation is linear with radiation dose up to about 10 Mrad. The peroxide is therefore a primary product of irradiation. It can be separated quantitatively (as an amorphous uncrystallizable solid) by its insolubility in petroleum ether. Homogeneity was inferred by chromatography although no crystalline derivatives were obtainable.

The peroxide has active oxygen values of $3{\cdot}0 \pm 0{\cdot}2$ (iodide method) and $3{\cdot}65 \pm 0{\cdot}05$ m equiv. oxygen per gramme (ferrous thiocyanate method). Molecular weight determinations and elemental analysis indicate a highly oxygenated system. Spectral data, perbenzoic acid titration and hydrogenation of the peroxide are in reasonable agreement with the presence of at least one double bond (side-chain), one peroxide group, a carbonyl group and the 3-hydroxyl group. The nature of the peroxide group has not been established. Its rapid reduction by ferrous ion and slow reduction (at 20°) by iodide ion favour respectively hydroperoxide and disubstituted peroxide structures.

The radiation-induced oxidations of ergosterol and calciferol probably proceed by a free radical chain process since the *G*-value (molecules/100 eV) for product formation exceeds 20 in both cases. Such a mechanism and the relative stabilities to radiation of the two types of steroids viz. the hormones containing the —C=C—C=O group and the unsaturated "hydrocarbon" types (—C=C—C=C—) such as ergosterol and calciferol, are in agreement with conclusions derived from electron spin resonance studies.[8] Apparently carbonyl groups may act as protectors against oxygen attack on free radicals in certain irradiated substances.

The use of ionizing energy as an aid in the exchange tritium labelling of organic compounds has recently been noted[9] (cf. Ref. 10 for effect of recoil tritium and neutrons on a steroid in air).

Cursory studies on ergosterol and calciferol in benzene solution revealed that γ-induced changes can proceed rapidly at low energy input. Spectral data suggest that the changes are comparable with known photochemical transformations of these alcohols (e.g. formation of toxisterols).

Acknowledgements—Gifts of steroids from Glaxo Laboratories Ltd. and British Drug Houses Ltd., are gratefully acknowledged.

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Influence of the Humidity on the Spark Formation in Rosenblum Counters

(*Received* 22 *January* 1960)

THE efficiency of the spark counters in air (Rosenblum type) depends largely on the water vapour content of the air.[1,2] A set of measures[1], performed with humidity up to 27 mm Hg, has shown a noticeable improvement of the efficiency with humidity increase in the case of irradiation with α-particles in end-on direction (perpendicular to wire and rod in their plane) but no improvement for broad-side irradiation (perpendicular to the plane of the electrodes axis).

We have experimented with wire-rod counters in air, detecting the α-particles of a Po^{210} source placed at about 34 mm from the wire. In this manner we have been able to take advantage of the maximum specific ionizing power, obtaining a good efficiency for broad-side irradiation also. The trial has been carried out in saturated environment at various temperatures (up to 56·2°C, which corresponds to the saturation pressure of about 125 mm Hg). Such a procedure may be followed because the counter efficiency becomes practically independent of the temperature.

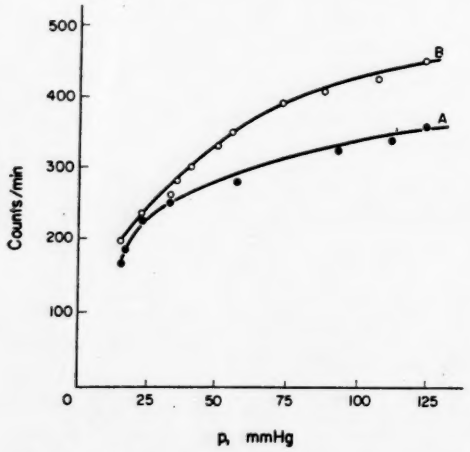

FIG. 1. Curves counts/min. vs. water vapour pressure. Curve *A*: broad-side irradiation with 1 mm gap. Curve *B*: end-on irradiation with 1·5 mm gap.

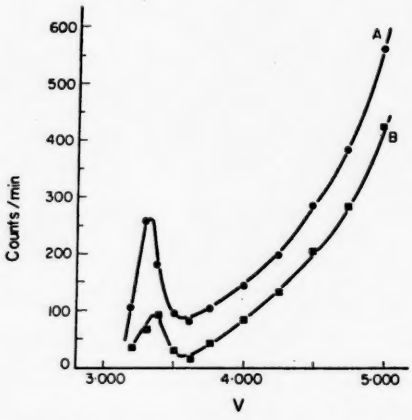

FIG. 2. Curves counts/min vs. applied potential. Curve *A*: water vapour pressure 112 mm Hg. Curve *B*: water vapour pressure 27 mm Hg. Gap 1·5 mm.

Some of our results are reported in Figs. 1 and 2. In Fig. 1 one may see the dependence of the efficiency with humidity from 15 to 125 mm Hg, for broad-side and end-on irradiation, for particular values of applied voltage and for two counters of different construction characteristics. In Fig. 2 one can see the plot of counts/min against applied voltage curves for broad-side irradiation for two different values of water vapour pressure.

Discussion of results

For the interpretation of this effect one must bear in mind that the humidity hinders the spark when it occurs as a Townsend mechanism[3], and favours it when it occurs as a streamer[4,5]. The first effect is attributed to the fact that humidity augments the negative ions, which diminish the final charge of every avalanche. The second effect[5] is attributed to the photo-ionization of the molecules of water vapour by ultra-violet photons produced in the course of the discharge.

These facts seem to confirm that the spark mechanism in our counters is of the streamer type. Such a streamer must be considered to be triggered by several initial avalanches developing in the sensible volume, along the path of an α-particle.[2] In a quantitative treatment to justify all the experimental evidences we should however take into account the lesser mobility and diffusion of attached electrons with respect to free electrons.

Acknowledgement—We are grateful to Professor T. FRANZINI for his stimulating discussions and his helpful advice.

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Assay of $C^{14}O_2$ in Geiger Counters

(*Received* 3 *March* 1960)

THE most commonly used method for the assay of $C^{14}O_2$ is to introduce the gas as part of the filling of a Geiger counter with CS_2 as an exchange gas and to use an electronic quenching unit with a dead time of about 1 msec.[1-3] This method has the disadvantages that CS_2 is an unpleasant and inconvenient liquid to handle, that special electronic equipment is required, and that the long dead time severely limits the maximum counting rate.

The use of alcohol as a quenching and exchange gas in resistance-quenched Geiger counters with CO_2 fillings has also been described[4-7], but a self-quenching filling with an external quench unit giving a short fixed dead time, for coincidence corrections only, is more desirable. To investigate this arrangement a probe unit* with a fixed dead time of 400 μsec and a counter,† of sensitive volume 50 ml and with a stainless-steel cathode and pyrex glass envelope, were used.

In preliminary measurements, ethyl formate, ethyl alcohol and toluene were used alternatively as quenching agents at 1 cm pressure with $C^{14}O_2$ at 10–15 cm Hg. Although plateaux from 300 to 400 V long, with starting potentials in the neighbourhood of 2500 V, were obtained when using ethyl formate and toluene, the plateau slopes were respectively 4 and 5 per cent/100 V. With alcohol as quenching agent, the plateaux were 160 V long or less, but slopes of 2 per cent/100 V or less were obtained. From this preliminary work it was decided that the more clearly defined plateaux of small slope but limited length obtained using alcohol, would be more suitable for comparative measurements, and no further work was undertaken to try and improve the results using toluene or ethyl formate.

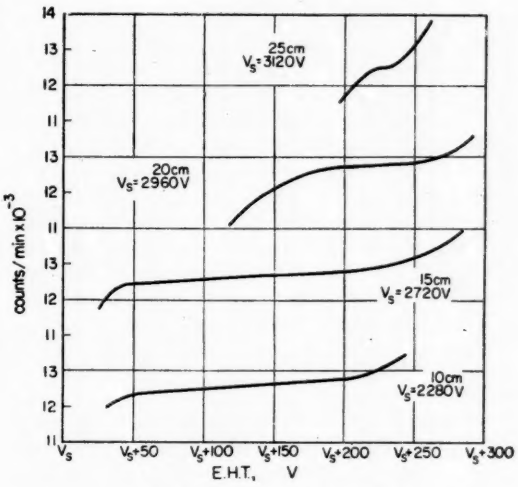

FIG. 1. Characteristic curves of CO_2–alcohol fillings with various total pressures (1 cm alcohol).

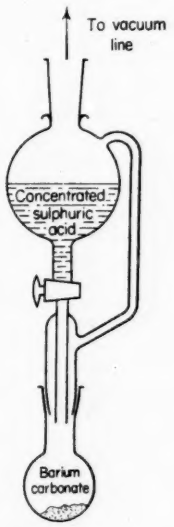

FIG. 2. Apparatus for preparation of CO_2.

* Harwell type 1014A.
† Twentieth Century Electronics Ltd. Type GA10M.

The effect of increasing the partial pressure of CO_2 with an alcohol pressure of 1 cm is shown in Fig. 1. It is seen that the plateau length decreases sharply with increasing pressure of CO_2, being non-existent when the CO_2 pressure reaches 25 cm. The optimum pressure of 10 to 15 cm of $C^{14}O_2$ limits the ultimate sensitivity of the method. Provided that the partial pressure of alcohol is above 5 mm, its value has little effect on the plateau slope, though the starting potential does increase with alcohol pressure. For the preparation of the $C^{14}O_2$ from labelled barium carbonate, the apparatus shown in Fig. 2 is used. The small flask containing the barium carbonate is attached to the bulb containing concentrated sulphuric acid and the whole evacuated to about 1 mm pressure; too low a pressure results in such a vigorous reaction that some of the barium carbonate is blown out of the reaction vessel.

The acid is allowed to drip slowly onto the carbonate and an adjacent cold finger, cooled with liquid nitrogen, collects the $C^{14}O_2$ generated, together with some water. After the completion of the reaction this apparatus is isolated and the cold finger is opened to the main line and pumped to remove the remaining traces of air. A second cold finger is situated further along the vacuum line, and between the two is a cooling coil surrounded by an acetone–dry-ice bath. This removes the water content as the $C^{14}O_2$ is passed to the second cold finger.

This pure dry sample of $C^{14}O_2$ is then expanded into a counter previously filled with the quenching vapour and the mixture is left for 5 min before counting.

Except when very high sensitivity or absolute measurements were required, this relatively simple procedure for the assay of $C^{14}O_2$ has proved quite satisfactory. The reproducibility on repeated measurements of the labelled barium carbonate was better than 2 per cent and no contamination of the counter between filling was observed.

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letters to the editors

Biological Fractionation of Isotopes

(*Received* 12 *May* 1960)

In his recent review[1] on this subject Bowen refers to a paper of ours[2] and says that "we have shown that tritium is used less readily than deuterium in lipid metabolism of unweaned rats". We did not in fact draw this conclusion either in the preliminary report[2] or in the full paper[3] in which the results were discussed in detail.

In our experiments the body water of lactating rats was maintained at a fixed tritium-deuterium ratio for 14 days after which they and their pups were killed and fatty acids analysed for the two isotopes. In the fatty acids of the maternal mammary glands and in the fatty acids of the pup carcasses the tritium-deuterium ratio was only 77–80 per cent of that in the maternal body water.

The relatively low tritium content of the fatty acids of the pup carcasses could have been the result of one of two processes. First there might have been considerable net synthesis from small molecules in the pups themselves during which isotopic fractionation occurred. This is the mechanism mentioned by Bowen. Alternatively their carcass fat could have been derived mainly or wholly from milk fat already containing the reduced isotope ratio. In the experiments reported there was no means of deciding between these alternatives although we thought that the latter was more likely.

A more interesting aspect of the results not mentioned in Bowen's review is their relevance to our hypothesis[3] that isotopic fractionation in tissue constituents occurs only during net synthesis and not during turnover. Net synthesis of fatty acids from small molecules (including water) is characteristic of the lactating mammary gland whereas turnover of fatty acids is believed to predominate in the liver. The finding of much more isotopic fractionation in the fatty acids from mammary gland than in those from liver supported our hypothesis. Results with liver fatty acids in quantitative agreement with ours (i.e. little or no fractionation) have been obtained by Eidinoff, Perri, Knoll, Marano and Arnheim[4]. We suggested also that our hypothesis might explain the small degree of fractionation found by Thompson and Ballou[5]. Most of their samples consisted of pieces of tissue such as muscle, pelt, brain, liver, and residual carcass in which net synthesis was not likely to have been very active.

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Wellcome Research Laboratories Beckenham, Kent — W. G. Duncombe

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book reviews

International Directory of Radioisotopes—I. *Unprocessed and Processed Radioisotope Preparations and Special Radiation Sources.* International Atomic Energy Agency, Vienna 1959.

THE purpose of this International Directory as stated in the Preface, is to collect together information on radioisotopes, including radiation data, sources of supply, prices and ordering procedure. It fulfils this object very well. This volume contains tables of available radioisotopes and special solid sources and will be followed by a separate volume listing labelled compounds of C^{14}, H^3, I^{131}, P^{32} and S^{35}.

The short introduction to the safe handling of isotopes is extracted from a previous useful I.A.E.A. publication (*Safe Handling of Radioisotopes*, I.A.E.A. Safety Series No. 1, Vienna 1958).

A complete list of suppliers of isotopes includes details of irradiation facilities and neutron flux. It does not give any information on the size or volume of standard irradiation containers or the maximum size of objects which can be irradiated. The marketing of isotopes in the United Kingdom should now be shown under the Radiochemical Centre, Amersham and not A.E.R.E., Harwell.

An explanation of the terms used in the Directory precedes the comprehensive list of radioisotopes which gives details of the standard weight and chemical composition of irradiation units and the specific activity of the product available from many suppliers. The cost is given in local currency and U.S. dollars. The half-life and radiation data appear to be taken from a draft copy of Radioisotope Data, A.E.R.E. Report 2938 and a notable error in both publications is in the figures given for the gamma radiation from Ca^{47} which should read 0·48 MeV (5 per cent), 0·83 MeV (5 per cent), 1·31 MeV (78 per cent).

This Directory collates the technical and sales information from the many member countries of the International Agency and includes details of the products of most of the commercial suppliers throughout the world. It is very well produced and will be most useful to anyone wishing to purchase radioisotopes.

D. B. SMITH

Proceedings of the Second International Conference on the Peaceful Uses of Atomic Energy. Vol. 19—*The Use of Isotopes: Industrial Use.* United Nations, New York 1958. 366 pp., 89*s*.

THIS is a volume which can be recommended to all existing or potential industrial users of radioactive isotopes. It contains 52 papers from 19 countries which both survey the general industrial uses of isotopes and also give detailed examples of up to date research.

The first portion of the book consists of general survey papers which indicate the increasing industrial use of radioactivity in industry. The stress is not so much on research as on the successful results obtained in large scale industrial investigations with radioactive tracers. Most of the techniques are already established but there is much of interest in the individual investigations into mixing, detention times, gas and liquid leaks, moisture content measurements, density gauges and many other applications. One medical paper seems to have strayed into the wrong volume.

The second part of the volume contains up to date research papers together with further general reviews. Some of the notable work which is reported here includes the increasing use of bremsstrahlung sources in the identification of elements by fluorescent excitation of the characteristic X-rays, the use of a portable neutron generator (using the *D-T* reaction) to activate oxygen by the O^{16} (n, p) N^{16} reaction and using the 7·4 second nitrogen to measure water flow rates, and the measurement of flow-rate in rivers or pipes by recording the integrated count as a pulse of radioactivity passes the counter. The use of autoradiography in metallurgical and surface studies is well illustrated as is the use of new isotopes for low energy radiography.

A short discussion is included after each of the two sections of the book and it is very unfortunate that more time was not devoted to this at the Conference since it makes very stimulating reading.

The collection of references in this volume is extremely valuable since the industrial applications of radioactivity are reported in a very wide range of

journals. It is unfortunate that a book containing such a wealth of scattered information has no index. In spite of this, it is a very valuable reference book on up to date radioisotope applications and is highly recommended for the bookshelf.

D. B. SMITH

Syntheses of Heterocyclic Compounds. Volumes 1 and 2. Edited by A. L. MNDZHOIAN. (Translated from the Russian by A. E. STUBBS.) Consultants Bureau, Inc., New York; Chapman and Hall London, 1959. 84 pp., 48*s*.

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THE object of this series of volumes is to collect thoroughly tested methods for the preparation of heterocyclic compounds. The first two volumes, which are bound together in the English translation, are devoted entirely to furan derivatives and it is planned to deal with other heterocyclic systems in later parts.

This series is clearly intended to be the heterocyclic *Organic Syntheses* and should be measured by that yard-stick. The layout in *Syntheses of Heterocyclic Compounds* follows closely the familar one in *Organic Syntheses*. Indeed, several of the preparations described in the Russian book were drawn originally from this source and have undergone the roundabout process of translation from English into Russian for the 1956–57 Russian edition of *Organic Syntheses* and now back again into English. These preparations appear again essentially as they did in the original English. Most of the syntheses, however, are based upon Russian work; this makes the book welcome since previously inaccessible material is now readily available to chemists outside the U.S.S.R. Experimental directions are given for many useful substances, but there are several reactions which could have been replaced with advantage by different ones since they are very similar to others in this volume. In one case the best method has not been selected; 2-furanpropionic acid is prepared by a sodium amalgam reduction which is surely much less convenient than a simple catalytic hydrogenation which gives high yields.*

The presentation of the book is good and only a few minor errors were found. Even in its more limited field, *Syntheses of Heterocyclic Compounds* is not the equal of *Organic Syntheses* but for chemists specializing in furan chemistry it is a useful book and one which they will wish to buy.

A. R. BATTERSBY

* *J. Chem. Soc. Lond.* p. 618 (1953).

N. VEALL and H. VETTER: **Radioisotope Techniques in Clinical Research and Diagnosis.** Butterworths, 417 pp., 50*s*.†

THE authors of this book have attempted to provide a complete general guide, of reasonable length, for those undertaking work with radioactive tracers in the medical field. This is an important objective which, in the opinion of the reviewer, they have fully achieved.

Mr. Veall has been associated with this field since it began and has made many original contributions to it. Dr. Vetter also worked with him early on and is now with the International Atomic Energy Agency in Vienna. It is this circumstance which gives their book its especial value: going through the text one senses that here are two people who really know, as the fruit of continuous experience at the bench, what the problems are in this technique, which is so easily rushed into and so difficult to apply well. Their chapters have, as a result, a reassuring down-to-earth flavour. They are also clear and readable and the writing is occasionally enlivened with gentle touches of sarcastic humour which encourage further reading. There is little of that disjointedness which so often mars collective writing. The diagrams and tables are plentiful and excellent; the photographs are occasionally a little dated.

No consideration of importance to those starting up an isotope service is omitted. Details of isotope supply, electronic instruments and radiation detectors are to be found, as well as chapters on radiation dosimetry, radiochemical procedures and isotope practice. As a result a balanced picture of the isotope technique emerges which, because of the authors' constant emphasis on practical considerations, is almost a living one. They do not make the mistake of seeing the subject as a specialized branch of physics, but give chemistry and biology their due weight. Each chapter has an adequate list of references, more comprehensive in some cases than in others, the authors' predilections showing up markedly here. Not the least valuable feature is a magnificent analytical index; quite obviously they have gone to great trouble to produce this and by doing so have probably doubled the value of the book.

Any author who dares to try to cover the whole of this field is bound to produce a work which is a little thin in places. This is true, I think, of the sections on radiation hazard, for example, where a lengthier and more discursive treatment would have been good education. On the other hand, in fields which the authors have to some extent made their own, such as

† *Radioisotopen Technik in der Klinischen Forschung und Diagnostik*. (Translated by R. Wittenzellner). Urban & Schwarzenberg, München, Berlin. DM 48.

circulation studies and blood volume, the text is authoritative.

Only one significant error was noted. On p. 151 a formula is given for the absorbed dose-rate of β-rays in tissue:

$$R_\beta = 2{\cdot}25\ C\bar{E}_\beta \text{ rad/hr.}$$

The figure should be 2·13; the calculation is simple and is given in Hine and Brownell's standard work (*Radiation Dosimetry*, p. 824).

The book fills an important gap and is at least as useful for teaching purposes as it is in the laboratory.

D. G. ARNOTT

Low Level Irradiation. Edited by AUSTIN M. BRUES. A symposium presented at the Indianapolis Meeting, December 30, 1957, American Association for the Advancement of Science (Publication No. 59), Washington, 1959. x + 148 pp.

THE purpose of the symposium which is reported in this book was to discuss biological radiation effects at low levels both from a scientific standpoint and from the standpoint of related problems, such as those of the press, of public health authorities, statesmen and philosophers interested in "the true role of science". Although more than 2 years have passed since the material was presented, as is often the case, the discussion is not greatly different, so far as our current knowledge is concerned, from more recent discussions of this subject. More up-to-date information has been inserted and mentioned in the summary by the Editor. The book therefore presents relatively current summaries of scientific information and discussions of its implications in a pleasant and easily understandable form by well qualified persons.

In Part I, "Scientific Background", following a brief summary of the problems by E. L. Powers of Argonne National Laboratory, a discussion of natural and artificial radiation in man is presented by Robert A. Dudley of the Massachusetts Institute of Technology. Natural radioisotopes, cosmic rays, fall-out and medical irradiation are discussed, and dose rates to the gonads and skeleton from each are estimated (1957). He points out that future uses of atomic energy present problems equally as important as fall-out.

Lester Machta of the U.S. Weather Bureau presents a discussion of facts and theories on the distribution of radioactive fall-out from nuclear tests much of which has since been confirmed or strengthened by more recent data. Fall-out resulting from a nuclear war is also mentioned.

Genetic effects of radiation are presented by Earl L. Green of the Roscoe B. Jackson Memorial Laboratory. This much-discussed but complex subject is presented concisely with emphasis on (1) a threshold, (2) cumulative effects, (3) homozygotes and heterozygotes, (4) breeding structure and (5) quantitative traits. In summary, Dr. Green remarks, "Perhaps most importantly, we need to devise adequate but not overwhelmingly expensive methods of assessing the genetic health of the present human populations of the world. Not until we do so can we detect changes in the population and, on the basis of theory and experimentation, predict what course the changes will take". AUSTIN M. BRUES of Argonne National Laboratory and Editor of the book concludes Part I with a discussion of "somatic effects". He points out the difficulties in observing quantitatively possible relations between low doses and effects, as has Dr. Green for the genetic problems. He mentions theoretical approaches to the problem as well as available experimental evidence. Using the few data available for leukemia, he shows how a number of different but reasonable dose-effect curves "may be drawn through a few uncertain points" and remarks that a single hypothesis should not be selected too quickly.

Part II, "Implications", deals with the largely nonscientific problems related to the low-level irradiation problem. David E. Price of the U.S. Public Health Service discusses radiation as a public health problem, emphasizing the necessity for prevention of unnecessary exposure. A considerable effort has been made by health agencies to reduce needless X-ray exposure while maintaining its benefits. The three main problems to the public health profession are (1) to alert the public, (2) to train health personnel and (3) research. Arthur J. Snider of the Chicago Daily News presents a discussion of the responsibilities of the press as related to low-level irradiation which is essentially to present the latest available information to the public. He discusses the secrecy which has surrounded information in the atomic energy field. He also discusses the subjects of sensational press reports, problems inherent in news publication, reader response and the reluctance of many scientists to "descend from ivory towers to co-operate with the press."

Legal and political implications are presented by the Honorable Chet Holifield, House of Representatives, and Chairman of the Special Sub-committee on Radiation of the Joint Committee on Atomic Energy. He summarizes the many problems in this connection which must be considered by the Federal and state governments and a number of international agencies. Problems of protection from radiation injuries, federal and state regulations and international aspects of the

problem are discussed. C. West Churchman of the University of California concludes Part II with a philosophical discussion of Science and Morality. The institution of science and the moral code of science are the primary subjects of the presentation and he presents questions deserving of much thought by scientists in general. In conclusion he remarks, "If scientists don't do their own planning, somebody else will do it for them".

A. W. KLEMENT, JR.

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NOTICE

"The Review Department of our medical periodicals is of all the most defective. There are a few honorable exceptions, but the large majority afford little more than a few meager pages of booksellers' notices, serving to advertise the work whose title is given, and seldom affording any impression whatever of the character and contents of the book named."*

In looking over the book reviews from many journals (especially technical journals but also in non-technical publications) my colleagues and I find that they are of such widely varying value that we think they should be standardized, although the word "standardized" is absolutely the wrong word to use in this context. There should be no "standardization" and nobody should attempt to instruct a book reviewer on what he should or should not say. Nevertheless, reviews are so frequently both unimaginative and uninformative that something has to be done about them. Some book reviews are exceedingly interesting to read but explain little about the book reviewed. Others tell a great deal about the book, but are dull. Some reviews are taken directly from the publicity fly-leaves and are neither informative nor interesting. We think a review should contain certain minimum information and we are listing this as follows in what we think is the order of precedence of each item.

1. *Title and description*

   (a) Title of book
   (b) Author(s)
   (c) Publisher
   (d) Price
   (e) Number of pages
   (f) Number of illustrations
   (g) Special information on procurement, if this is indicated.

2. *The reviewer*

   (a) Name
   (b) Title or at least a one-line statement of the reviewer's qualifications to review the book.

We think it is exceedingly important that, since we are asking the reviewer to give an opinion, we know who the reviewer is and his qualifications. Usually we will not know the reviewer by name and it is impossible for us to make a decision concerning his opinion unless we have some idea of his qualifications.

3. *The authors*

We think that all reviews should commence by telling the reader something about the authors of the document. This should not be a biography but should be sufficient to inform the reader of the author's qualifications to write and to discuss the subject matter.

4. *Description of the content*

In describing the content and subject matter of a document the reviewer should enable the reader to determine that the book is a textbook, or a proceedings, or a review of a whole subject, or a description of a completely new subject, or a report of a research project. The description of the content should describe exactly what is covered in the book without any bias on the part of the reviewer, and not be just a table of contents.

5. *Biases in the subject matter*

Hardly anyone can write on any subject without having some bias. The reviewer's job is to describe this bias. The fact that there is also a bias in determining somebody else's bias is the reason why it is just as important to have a knowledge of the reviewer as it is to have a knowledge of the author! In describing the bias of the document, we are asking for the reviewer's opinions and it should be expected that they will be biased.

6. *Techniques of publication*

At the reviewer's discretion a short statement should answer the following questions if they are pertinent: Is the document mimeographed or printed? Are there many or few typographical errors? Are the illustrations well or poorly reproduced? Are there sufficient illustrations? Were the references checked? Does the index check with the subject matter? Is the table of contents useful or just another wasted page? Are there sufficient sub-headings? Is it easy to read? Is it small type on tissue paper or is it large type on semimat paper?

7. *The style of writing*

One of the most important things that a reviewer can and should pay attention to is the author's style.

* A Report of the Sixth Annual Meeting of the American Medical Association, *New York Daily Times*, Vol. 2, No. 510, p. 1, Friday 6 May 1853.

Is the book interesting to read? Is it readable to a grammar school student, a high school student, a college student, or only to an expert in the particular field that is being covered?

8. *The summary opinion of the reviewer*

Most people have little time to read everything published in their own fields of special interest, let alone sufficient time to read everything in every field. We need help in deciding what we do and what we do not want to read. For this reason the reviewer should give his opinion of how the document compares with other documents in the field. For example, in reviewing textbooks it might be the reviewer's opinion that this is "just another textbook." Or it might be his opinion that this is "the best textbook." Or it might be his opinion that it is an inadequate textbook. This is an important part of the review. A reviewer should state his honest opinion in a straightforward manner. People who read book reviews are reading them because they don't have time to read the full book or they are trying to find out whether they should purchase the book or not.

9. *Size of the review*

An exceedingly important part of all reviews is—*what size should the review be?* We think a review should be about 200 to 1000 words. Shorter ones are generally inadequate; longer ones may become merely tedious. The shorter a review, the better it is (usually).

MARSHALL BRUCER

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Abstracts of Papers Presented at the International Atomic Energy Agency Conference on the Use of Radioisotopes in the Physical Sciences and Industry

Copenhagen, 6–17 September 1960

Application of Tritiated Water as a Tracer for Quantitative Determination of Water Flow Distribution in an Oil Field. E. KUYPER and H. NAUTA, Koninklijke Shell Laboratories, Amsterdam, Netherlands

In order to study the flow of water in an oil reservoir, tritiated water was injected in a well and subsequently tritium was determined in the water produced by the surrounding wells. Since the specific radioactivity of the water produced by the more remote wells appeared to be rather low, partly owing to dilution of the tritium water by the water present in the formation, enrichment methods were used. The tritium was determined with a liquid scintillation counter; the scintillator consisted of a toluene ethanol (2:1) mixture with DPO and POPOP, the water sample being dissolved in this liquid. An increase in sensitivity was obtained by the following methods:

1. Direct tritium exchange between sample water and ethanol. The sensitivity gain, however, is rather poor in this case, approximately by a factor 3.

2. Conversion of the tritium water by a Grignard synthesis into toluene, the tritiated toluene being used as a solvent for the scintillator. By this procedure not only the tritium concentration in the scintillator is raised but also the efficiency of the tritium-beta-ray detection. A sensitivity gain of 8 has been found.

3. Enrichment of tritium in the water sample by electrolysis. The water was rendered conducting by adding sulphuric acid. The enriched water was used in the scintillator without removal of the H_2SO_4. An enrichment factor of 30 is easily attainable in one stage.

Some statistical problems in connexion with the minimum detectable specific activity and the reduction of background will be discussed briefly.

Tracer Investigation of the Fate of Sulphur Atoms in the Course of High Temperature Reactions. A. H. W. ATEN, Stichting Instituut voor Kernphysisch Onderzoek, Amsterdam, Netherlands

The fact that sulphur occurs in many different chemical conditions suggests a number of interesting problems in connexion with the movement of the sulphur atoms in the course of reactions between different compounds of this element. Quite an amount of information is available concerning reactions between compounds of sulphur in solution and in general the different sulphur fractions do not mix under these conditions.

An entirely different situation is found in reactions between gases and solid compounds. For these processes much higher temperatures are in general required and at these higher temperatures the sulphur atoms in the different fractions tend to mix to a very large extent. This behaviour is illustrated by means of data obtained on the exchange of radiosulphur between sulphur vapour and sulphur dioxide, between sulphur dioxide and solid sulphite and between sulphur dioxide and solid sulphate. The same behaviour has been observed in the chemical decomposition of thiosulphate, labelled in one of the two sulphur fractions and in the oxidation of this compound. Finally, it has been shown that mixing is very strong too in the reaction between sulphur vapour and solid sulphate.

Treatment of Solutions of Fission Products Separation of Caesium-137. R. STIENNON-BOVY, Centre d'études pour les applications de l'énergie nucléaire, Mol, Belgium, and R. GVION, Atomic Energy Commission, Tel-Aviv, Israel

For the industrial recovery of Caesium-137 from solutions of fission products we utilized the analytical method for determination of caesium by dipicrylamine, adapting it to use on an industrial scale and to the high level of the activities encountered.

The process we recommend makes it possible both to isolate caesium as a chloride and to recover the reagent, in one and the same operation. We suggest a basic method, that may be varied according to the acceptable activity level of the residues. We studied the effect of radiation on dipicrylamine and its compounds, this effect proving to be practically nil for solid compounds and negligible for their solutions. The entrainment of caesium by ammonia ion was also studied.

The advantages of the proposed process are:

high decontamination of the caesium;
simple operation and free recycling of the reagent;
high yield for caesium recovery and for dipicrylamine;
considerable concentration of caesium activity;
operation at room temperature;
possibility of continuous operation.

By this process caesium can be recovered before certain fission products are eliminated.

Synthesis of Methyl 3-O-a-D-Glucopyranosyl-C_6^{14}-p-D-xylopyranoside and Methyl 2-O-a-D-Glucopyranosyl-C_6^{14}-L-novio-pyranoside. S. A. BARKER, M. C. KEITH, M. STACEY and D. STROUD, Chemistry Department, University of Birmingham, Birmingham, U.K.

Where difficulty is encountered in the chemical synthesis of a disaccharide glycoside labelled with C^{14} specifically in only one of its sugar moieties it is often convenient to resort to a synthesis catalysed by microbial transglycosylases. We wish to report, as two examples of the application of this technique, the following syntheses:—

Maltose-C_{12}^{14} + Methyl *p*-D-xylopyranoside

$$\xrightarrow[\text{transglucosylase}]{\text{Penicilium lilacinum}}$$

Methyl 3-O-a-D-Glucopyranosyl-C_6^{14}-*p*-D-xylopyrano-side(I) + Glucose-C_6^{14}

Maltose-C_{12}^{14} + Methyl-L-noviopyranoside

$$\xrightarrow[\text{transglucosylase}]{\text{Fusarium moniliforme}}$$

Methyl-2-O-a-D-Glucopyranosyl-C_6^{14}-L-noviopyrano-side(II) + Glucose-C_6^{14}.

In such syntheses it is predictable that the anomeric character of the glycosidic linkage of the donor disaccharide (in the case of maltose the *a*-configuration) will be retained in the disaccharide synthesized (I or II) and that the glycosyl residue transferred will be attached through its reducing group (in these cases C_1) to the receptor monosaccharide glycoside (e.g. methyl D-xyloside or methyl L-novioside). By using either a C^{14}-labelled donor disaccharide or a C^{14}-labelled receptor glycoside, a disaccharide can be synthesized with only one of its sugar moieties labelled. In the synthesis of II the only hydroxyl group free in the receptor methyl novioside (methyl 3-O-carbamyl 4-O-methyl-5, 5-dimethyl-L-lyxoside) is on C_2 and the transferred glucosyl residue can only be attached here. In the synthesis of I the methyl xyloside has free hydroxyls on C_2, C_3 and C_4 and the microbial enzyme has been found to transfer the glucosyl residue specifically to the hydroxyl on C_3. The structures of I and II have been established by the results of elemental analysis, optical rotation, infra-red spectra together with an examination of the products of acid hydrolysis and periodate oxidation.

The Determination of Sulphur in Materials of High Neutron Absorption Cross-section by Fast Neutron Activation Analysis. D. GIBBONS and H. SIMPSON, U.K. Atomic Energy Authority, Atomic Energy Research Establishment, Harwell, Didcot, U.K.

The production of radiophosphorus by the fast neutron (n, p) reaction on sulphur is used for the determination of sulphur by activation analysis. Using this technique it is possible to determine sulphur in materials of high thermal neutron absorption cross-section because the absorption cross-sections for fast neutrons are, in general, much lower than those for slow neutrons, so that self-shielding errors are considerably reduced. Interference due to the slow neutron (n, y) reaction on natural phosphorus is eliminated by a double irradiation technique involving irradiation in regions of differing slow/fast flux ratios.

The method has been applied to the determination of sulphur in chromium and arsenic.

Symmetrical Exchange Reactions Between O-Acetylglycosyl Bromides and Lithium Radiobromide in Acetone. G. O. PHILLIPS and A. BRIGHT, Department of Chemistry, University College, Cathays Park, Cardiff, U.K.

Kinetic experiments on the bromine exchange reactions between the O-acetylglycosyl bromides and lithium radio-bromide (prepared from $NH_4{}^{82}Br$) in acetone are reported. For tetra-O-acetyl-α-D-glucosyl bromide and the corresponding D-galactose, D-mannose, D-xylose bromides, the results indicate that exchange proceeds by way of a bimolecular mechanism (S_N2). Second-order kinetics are observed, and increasing the ionizing power of the medium leads to a decrease in reaction rate. A negative salt effect, characteristic of bimolecular halogen exchange reactions in acetone, follows an increase in lithium radiobromide concentration.

As a result of structural changes, the reactivity of the O-acetylglycosyl bromides in the bimolecular reactions studied varies considerably. The rate variations are shown to be due to changes in energy of activation rather than changes in entropy.

Previously only unimolecular reactions (S_N1) have been established at the lactol carbon atom in the O-acylglycosyl bromides. The results now reported

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therefore make it possible to compare the effect of steric variations on S_N1 and S_N2 reactions without the disturbing influence of superimposed polar factors. Similar steric effects are shown by both mechanisms, due probably to the stringent requirements imposed by the sugar ring in the S_N1 reaction. This behaviour is not observed in aliphatic structures.

Identification and Estimation of Carbohydrates Using Radioisotopic Methods. G. O. PHILLIPS and W. J. CRIDDLE, Department of Chemistry, University College, Cathays Park, Cardiff, U.K.

Isotope dilution methods have been developed to identify and estimate the small amount of products formed when carbohydrates are irradiated in aqueous solution with ^{60}Co gamma-radiation. Conventional analytical methods proved inadequate.

After irradiation of ^{14}C-sugar solutions, the autoradiographs prepared after paper chromatography in butan-1-ol-acetic acid-water indicated extensive degradation. Using a reverse isotope dilution procedure involving the addition of known carriers, and conversion of the fragments into crystalline derivatives, the following constituents were quantitatively determined: D-glucose, D-mannose, D-sorbitol, D-fructose, D-arabinose, D-xylose, D-gluconic acid, D-mannonic acid, D-glucuronic acid, two- and three-carbon aldehydic fragments, sucrose, maltose and formaldehyde. It is possible to distinguish between D- and L-isomers, and estimate each isomer independently. The method is applicable to other analytical problems in carbohydrate chemistry.

The paper describes a new method for scanning and recording the radioactivity along paper chromatogram strip which involves an inexpensive modification to conventional counting equipment.

Continuous Analysis for Sulphur in a Refinery. R. PEGG and J. POLLOCK, Esso Research Limited, Abingdon, U.K.

A continuous plant analyser for sulphur, dependent on the absorption of X-rays produced by tritium, has been developed at the Esso Research Centre at Abingdon and has undergone satisfactory trials at Fawley Refinery.

The method depends on the very much greater absorption of soft X-radiation by sulphur atoms than by carbon and hydrogen atoms, so that small changes in sulphur content cause large changes in transmitted intensity. Gravity, carbon content and hydrogen content all affect the X-ray absorption. For a given refinery stream, their effects are small and constant compared with the much larger variations due to sulphur. In these circumstances, the effects may be offset electronically, and, because other heavy elements are not likely to be present, the new instrument therefore records sulphur content directly and continuously.

Experiments have shown that the instrument is capable of measuring sulphur levels between 0·05% and 1·0% in kerosines and gas oils with an accuracy of better than $\pm 0{\cdot}03\%$ sulphur. Plant trials showed that response time, stability and correlation with laboratory-determined sulphur contents were satisfactory.

Installation of this type of analyser should result in considerable financial savings by reducing plant upsets and by increasing throughput.

A Radioisotope Study of the Throughput of Glass Lubricant in Hot Extrusion of Stainless Steel. J. GOLDEN and G. W. ROWE, Tube Investments Research Laboratories, Cambridge, U.K.

The paper discusses the use of radioactive Na24 in sodium silicate, the material normally used for bonding glass powder, to measure the amount and distribution of glass coating on an extruded stainless steel hollow.

In common extrusion practice the bored billet is taken from the annealing furnace and rolled in glass powder to form a protective and lubricating skin. As it rolls, a supply of glass is poured into the bore to lubricate the extrusion mandrel. Finally the billet is placed in the press behind a pad of bonded glass powder, which provides the major source of lubricant during the extrusion immediately following.

Each source of glass is traced separately by applying the mixture of radioactive sodium silicate and powdered glass to the appropriate part and measuring the activity on the extruded hollows with a Geiger counter and with autoradiographs.

It is found that on an average hollow there is a reasonably uniform coating of glass about 75 microns thick over most of the surface, though the thickness decreases towards the trailing end, and there is a local reduction in thickness at a position corresponding to the original corner of the billet. The bore coating is also uniform except in this region. A small percentage of the initial coating of glass appears on the extruded hollow, contrary to earlier belief, and some remains in the container to appear on a second and even a third hollow.

The results suggest some improvements in extrusion and also show that it should be possible to use this technique to study in detail the influence on the glass coating of such variables as temperature, speed, glass composition and pad and die geometry. This should provide a valuable complement to the usual visual inspection.

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Beta-excited Sources of Electromagnetic Radiation. J. F. CAMERON and J. R. RHODES, Physics Group, Isotope Research Division, (AERE), Wantage Radiation Laboratory, Wantage, Berks, England

Beta-excited sources of electromagnetic radiation covering the energy region 0–200 keV and suitable for industrial use are described. ^{3}H, ^{147}Pm, ^{85}Kr, ^{204}Tl and ^{90}Sr–^{90}Y were chosen as sources of beta particles by the criteria of long half-life, low price, ready availability and high specific activity. The beta-excited sources have been designed on the basis of a compromise between practical source construction and the best theoretical efficiency in a given energy region.

The total intensities of bremsstrahlung and characteristic K X-radiation formed in a target material of atomic number Z by beta particles of maximum energy E MeV and root mean square energy E_{RMS} are given by:

$$E_{Brem} = 5{\cdot}8 \times 10^{-4}\, ZE^{2}_{RMS} + 3{\cdot}7 \times 10^{-1}E^{2} \quad \text{MeV photons/beta} \qquad (1)$$

$$M_K - 1{\cdot}5 \times 10^{6}Z^{-4}W_K E^{2}_{RMS} - E_K{}^{2} \quad K \text{ photons/beta} \qquad (2)$$

where E_{Brem} is the total bremsstrahlung energy formed and must be divided by the bremsstrahlung spectrum to obtain the total number of bremsstrahlung photons. M_K is the number of K X-ray photons, W_K the K shell fluorescent yield and E_K the energy of the K absorption edge. Characteristic X-ray formation is rarely as important as the accompanying bremsstrahlung because the X-ray to bremsstrahlung ratio is never much greater than unit and is often much less. Maximum X-ray yield is achieved for targets of 40 Z 60 because at low Z W_K is small and at high Z the yield is again low due to the Z^{-4} relationship in equation (2).

For practical purposes equation (1) and (2) must be corrected for self-absorption and it was found that the emitted bremsstrahlung yield and spectrum were changed radically by this. "Sandwich" targets of 1–2 beta half-value thicknesses were found to give optimum bremsstrahlung and X-ray yields in the desired energy region.

Al, Ag and Au are suitable from the manufacturing point of view as source coverings. They were also found to give satisfactory bremsstrahlung and X-ray yields and distribution for various energy regions in the range 0–200 keV when correctly combined with the above-mentioned beta emitters. Some energy spectra are given and absorption curves in Al and Fe are shown for the best source-target combinations. The difference between source constructed of beta-emitters sandwiched between target foils and intimate source-target mixtures was found to be small. Tables are given as a guide to the best source to be used for a particular absorber thickness range.

Leak Detection of Hermetically Sealed Components Using Kr^{85}. J. F. CAMERON and P. F. BERRY, Physics Group, Isotope Research Division (AERE), Wantage Radiation Laboratory, Wantage, U.K.

Radioactive gases provide a method of leak detection in hermetically sealed components which in specific cases can be more sensitive by several orders of magnitude than conventional methods of leak detection. In this paper the use of Kr^{85} for this purpose is described.

The gas can be used in two distinct ways. The first is to immerse the component in the gas under controlled conditions of pressure and time and measure the amount forced in under pressure by subsequent monitoring of the radiation transmitted through the walls of the component; in the case of walls of thickness greater than 250 mg/cm^2 this is a combination of Bremsstrahlung and gamma-rays. In the second method some active gas is inserted before sealing and the subsequent loss of activity is a measure of the leak rate. The method chosen depends on the dimensions of the component and its proposed use. Filling the component with even small quantities of radioactive gas is undesirable from a health point of view, although the amounts required often present a negligible hazard.

The chief limitation on the sensitivity in the first method is surface contamination due to absorption of the gas into the pores of the component material; the extent of this and the necessary corrections which have to be made are discussed in the application of the method to the detection of leaks in transistor cans. Allowing a time of one minute for monitoring each component, leak rates of the order of 10^{-13} cm^3 (NTP)/sec. are detectable and correlation of results achieved by this method with the manufacturers' tests for expected component life were made and the agreement was satisfactory. Generally speaking the larger the component the lower the sensitivity, so that to achieve 10^{-12} cm^3 (NTP)/sec., with thermionic valves it would be necessary to devote an hour to each measurement. Prefilling of the component with active gas before sealing has the advantage that, in addition to allowing an evacuation test and subsequent monitoring of the egressing gas to evaluate the leak rate with a sensitivity comparable with the helium mass spectrometer, a long-term monitoring of the contents of the component is possible. This eliminates the possibility of a leak closing up temporarily during the short term pressure or vacuum test and provides an integrated value to the leak which is more useful.

Direct Measurement of the Half-life of Rb^{87}. H. W. Wilson and A. McNair, Atomic Weapon Research Establishment, Aldermaston, U.K.

The half-life of Rb^{87} has been measured by two main methods. In the first, or geological, method the value is calculated from the ratio of radiogenic strontium to rubidium in a mineral of known age. In the second method, the specific activity is measured directly by a counting method. The half-lives obtained lie in the range $4–6 \times 10^{10}$ years, with a value of 5×10^{10} years being taken usually. Up till now most reliance has been placed on the geological method as the direct counting method is rather difficult, due to the presence of a large number of very low energy electrons in the Rb^{87} spectrum. However, it is clearly very desirable to obtain a precise value by the counting method and this we have tried to do.

In these measurements special attention must be paid to the reduction of thickness of source and of source backing. Also the apparatus must be able to detect very low energy electrons. The experiments to be described were very carefully carried out and it is believed that they yield a more reliable value for the half-life than those obtained previously by the counting method.

We have used the following methods to increase the accuracy of the measurements. The source thickness was reduced by use of (i) a 4π proportional counter of large source area (up to 100 cm^2), (ii) anticoincidence operation to reduce background, and (iii) enriched Rb^{87} which permits a four-fold reduction in source thickness for a given activity. By these methods, sources down to 2 micrograms/cm^2 have been measured. Also the relationship between half-life and source thickness was examined so that correction could be made for the very small absorption which remained. The effect of source backing thickness is not so great and can be calculated from (i) the difference in count rates on either side of the thin supports used and (ii) a study of dependence of half-life on source support thickness. These experiments give a value of about $4{\cdot}8 \times 10^{10}$ years for the half-life, and it is hoped that a more accurate value will be available in time for the meeting.

The Use of Tritium as a Static Eliminator at the 10–20 Curie Level of Activity. P. Reasbeck, Joseph Lucas Limited, Group Research Centre, Birmingham, U.K.

A difficult case of static electricity in a coil winding machine in which thin tissue paper is used as an insulation has been controlled with 10–20 curie sources of tritium absorbed into evaporated layers of titanium. The source is safe from the direct radiation point of view and also the re-emission of tritium is at a safe level. The system is described in detail.

The Limitations of Detection of Traces of Elements by Radioisotopes Fluorescence Spectroscopy. C. E. Mellish and J. A. Payne, U.K. Atomic Energy Authority, Atomic Energy Research Establishment, Harwell, Didcot, U.K.

In radioisotope fluorescence spectroscopy radioactive sources are used to excite characteristic X-rays from the specimens under investigation, and resolution of these X-rays is performed with a proportional or scintillation counter. The successful measurements of trace quantities by this method depends on the solution of the two problems of securing efficient excitation of the trace element X-rays and low scatter background from the specimens.

This low scattered background can only be achieved by using exciting sources with no high energy β particles or γ-photons; energies above about 60 KeV are extremely undesirable. Thus the present work has been confined to sources of Am-241, W-181, Cd-109, Fe-55 and H-3, all of which conform to this requirement.

Analytical measurements have been made on solutions, alloys, and minerals, and results are presented showing that in many cases it is possible to measure 0·1% of a minor constituent, and that under favourable conditions 10 micrograms of an element can be detected.

The Synthesis of the Insecticides Aldrin and Dieldrin Labelled with Carbon-14 at High Specific Activity. D. J. Thomas and A. E. Kilner, The Radiochemical Centre, Amersham, U.K.

Aldrin is the trade name given by Shell Chemicals to 1,2,3,4,10,10-hexachloro-1,4,4a,5,8a-hexahydro-exo-1,4-endo-5,8-dimethanonapthalene. Acetylene-1,2-C^{14} is converted successively to tetrachloroethane and trichlorocethylene, and this is condensed with carbon tetrachloride by the Prins reaction in presence of aluminium chloride to octachlorocyclopentene. Dechlorination gives hexachlorocyclopentadiene which undergoes a Diels-Alder addition to bicyclo-(2,2,1)hepta-2.5-diene to give aldrin-C14 in 12% yield from barium carbonate.

Oxidation of aldrin gives the 6,7 epoxide, dieldrin, in 87% yield.

The paper includes an account of the separation of octachlorocyclopentene from the crude product of the Prins reaction by gas-liquid chromatography and of the separation of aldrin and dieldrin on a small preparative scale by reversed phase paper chromatography.

The Application of Isotope Dilution Analysis to Studies with Optical Enantiomorphs. R. J. Bayly, The Radiochemical Centre, Amersham, U.K.

A brief description is given of studies on the racemisation of individual amino-acids in intact protein by treatment with dilute alkali. Using C-14 labelled protein it was possible to measure the amount of this racemisation by reverse isotope dilution analysis; of the amino-acids examined serine exhibited the phenomenon to the greatest degree.

Some figures are given indicating the applicability of this useful, but often neglected, method to various amino-acids.

Minor variations in the combination of mixtures of D- and L- forms can also be conveniently observed by means of isotopic labelling, and this is illustrated by studies on 60/40 mixtures of the enantiomorphs of threomine and of valine. The behaviour of the amino-acid which forms a racemote is readily distinguished from the one that does not.

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A Study of Inclusions and Segregation in Metals by Autoradiography. S. Makin, U.K. Atomic Energy Authority, Atomic Energy Research Establishment, Harwell, Didcot, U.K.

Three applications of radioisotope techniques to metallurgy are described. During the course of this work new autoradiographic techniques have been developed. These include the irradiation of autoradiography and extraction replicas, similar to those used in electron microscopy and a two-colour dye transfer process in which colour prints of autoradiographs are shown with the corresponding micrographs superposed.

These methods have been applied to the study of inclusions in steel and uranium and to an investigation of the segregation of sulphur and phosphorus in welds in stainless steel. Techniques developed in microphotometry and quantitative autoradiography are illustrated in a study of the concentration of fission products in some grain boundaries of a magnesium alloy.

Continuous Measurement of Gas Flow Using a Hinged Gate and a Radioactive Source. C. G. Clayton and J. W. Webb, Wantage Radiation Laboratory, Wantage, U.K.

The continuous measurement of volumetric flow of gas in turbulent and streamline condition is proposed using a small radioactive source mounted on a hinged gate.

The use of radioactivity enables measurement of the gate inclination to be made outside the pipe thus establishing the pattern of a simple instrument. The use of penetrating radiation also results in an extension of the operating range since it allows the advantages to be gained from using a multi-gate system; an external detector then gives simultaneous measurement of the resultant inclination of several gates.

Relationships between volume flow and detector current for single and multiple gate systems are given.

Dehydrocyclization of 2:2-Dimethyl-4-(Methyl-C^{14}) Pentane and 3-(Methyl-C^{14}) Heptane Over Chromia Alumina. F. R. Cannings, A. Fisher, J. F. Ford, P. D. Holmes and R. S. Smith (in part), The British Petroleum Company Limited, Sunbury, U.K.

The relative specific activities of the products obtained by processing the above C^{14}-labelled hydrocarbons over a potassium and cerium promoted chromia-alumina catalyst have been measured. Products were separated by gas chromatographic techniques, burnt to carbon dioxide and assayed as barium carbonate, using an end window Geiger-Müller tube. The distribution of radioactivity between side chain and ring in the aromatic products was assessed by dealkylation over fluorinated alumina catalyst and the distribution between α and β carbon atoms of ethylbenzene, produced from methylheptane, by de-alkylation to toluene and benzene over a nickel catalyst.

The results obtained with the first compound are consistent with an overall mechanism in which methyl groups at both ends of the molecule become attached at adjacent sites on the catalyst surface. Rearrangement at the trisubstituted end of the molecule to give a six membered ring, followed by dehydrogenation, gives *p*-xylene with 50% activity in the methyl groups. Toluene produced during cyclization has an activity distribution indicating that rearrangement also occurs to a lesser extent at the other end of the molecule.

The dehydrocyclization of methylheptane leads to the formation of the expected aromatics. However, the activity distribution shows that these have not arisen entirely by a simple ring closure mechanism; probable mechanisms are discussed.

The preparation of the labelled hydrocarbons on a one gram scale by a Grignard reaction using a novel decomposition step is also described.

The Use of Tritiofermaldehyde for the Autoradiographic Determination of the Distribution of Resins in Textiles and Tyre Cords. G. S. Park, Courtaulds Limited, Research Laboratory, Maidenhead, U.K.

Textile fabrics are often produced with anticrease and drip dry finishes by the formation of urea-fermaldehyde type resins in the material. It is

thought that the uniformity of the distribution of the resin within the material has an important effect on the utility of the fabric. To determine this distribution a high resolution autoradiographic method based on the low energy β particles from tritium was used.

Tritiofermaldehyde was synthesised photochemically from tritium gas and carbon monoxide and combined with urea to give a resin finish to a small piece of woven fabric. Portions of the fabric mounted in a "Perspex" block, sliced into sections and polished were used to give autoradiographs of the resin distribution. The high resolution obtained was sufficient to give the distribution of the resin within individual filaments. Simulating the normal commercial process it was found that the resin was uniform across any filament cross-section and no resin layer was observed on the filament surfaces. A deficiency of resin in the filament at the cross over points between warp and weft yarns was noticed and shown to be due to a migration during the drying process. Treatment from alcohol solution as well as certain other abnormal treatments gave a resin deposit on the surface and a gradient of resin concentration across a filament section. The autoradiographic method has been used to show the differences between the resin uptake of the different filaments in a blended fabric and has also been compared with a staining method for obtaining the resin distribution.

The distribution of the resorcinel-fermaldehyde adhesive used for bonding tyre cord to rubber has also been obtained with the aid of tritiofermaldehyde. The adhesive deposits in a thin layer on the surfaces of the filament throughout the whole cord. In the outer regions a slight penetration into the filaments was observed and a small amount was noticed between the filaments in the inner regions.

Some Symmetrical Halogen and Methoxy Exchange Reactions in Aromatic Systems. R. W. C. Broadbank, A. H. E. Harhash and S. Kanchanalai, Leicester College of Technology and Commerce, Leicester, U.K.

Isotopic tracers are essential in the study of the kinetics of symmetrical nucleophilic substitution reactions at an aromatic carbon atom.

The iodine exchange between iodo-nitro-aromatic compounds and iodide ions in acetone or methanol solution has been studied both qualitatively and quantitatively by labelling the iodide ions with iodine^{131}. The reaction mixture is sampled at convenient time intervals, the two reactions separated by toluene-water extraction, and the progress of the reaction ascertained by beta-counting with a liquid Geiger counter. Measurements have been extended to "carrier-free" concentrations of iodide ions.

The preparation of certain nitro-methoxy-aromatic compounds, labelled with carbon^{14} in the methoxy group, is described. Symmetrical methoxy exchange reactions of these compounds with methoxide ions, in methanol solution, have been studied. After separating the reactants (from samples of the reaction mixture taken at convenient time intervals) by toluene-water extraction, the aromatic compounds are recovered and their specific activities determined by beta-scintillation counting with a plastic phosphor.

In discussing the experimental data, special attention is paid to the effect of ionic strength on the specific rate of the reaction. Comparison is made with ionic strength effects observed in symmetrical bimolecular nucleophilic reactions at a saturated (aliphatic) carbon atom, and reference is made to certain other aromatic nucleophilic substitution reactions.

The Use of Radioactive Tracers in Lubrication and Wear Research. R. B. Campbell and L. Grunberg, National Engineering Laboratory, Thorntonhall, Glasgow, U.K.

In many lubrication and wear problems processes occurring on a very small scale have to be studied and the great sensitivity of radioactive tracer methods has been successfully applied. Several examples of such applications are cited from the work of the Lubrication and Wear Division of the National Engineering Laboratory in the United Kingdom.

The quantitative relation between metal transfer and boundary friction is studied as a function of sliding velocity, surface roughness and the presence of lubricants. In order to study the distribution of wear, cast iron plugs containing Ir^{192} are inserted in the linears of a diesel engine and the radioactivity present in oil samples is measured. Radioactive iron and iron oxide particles are used to study their role in the wear process. The reactivity of strained metal surfaces is studied with the aid of C^{14} labelled stearic acid and of S^{35} in solution. The reaction rates of gear oil additive is being studied by passing short electric current pulses through metal wires immersed in solutions of compounds labelled with S^{35} and P^{32}. The build up of anti-wear films on the surface of gear teeth is being studied as a function of lead, speed and running time.

A problem encountered in many of these applications is to the conversion of the measured activity into absolute quantities of materials present in surface films or in wear debris. Calibration methods have been developed for this purpose.

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Study of Reactions of Metals with Sulphur and Phosphorus Compounds by Pulsed Temperatures. R. B. CAMPBELL and L. GRUNBERG, National Engineering Laboratory, Thorntonhall, Glasgow, U.K.

The anti-wear action of sulphur and phosphorus compounds which are usually added to gear oils depends on chemical reactions with the metallic surfaces of the gears. These reactions occur both at the bulk oil temperature (approx. 100°C) and during high temperatures (approx. 600°C) of short duration when the gear teeth come into contact under lead. The temperature flashes were simulated in an apparatus in which short pulses of electric current were used to heat metal wires immersed in mineral oil containing S^{35} and P^{32} labelled compounds in solution. The radioactivity acquired by the wires was measured. The extent of the reactions was determined as a function of temperature and time and the results were interpreted in terms of conventional kinetic laws. The modification of the reaction rates by the presence of other compounds in the solution was studied. The effect of pre-formed surface films containing sulphur phosphorus, chlorine and/or oxygen was also determined. In explaining the results the structure of the materials used and the diffusion processes whereby the reactions occur beyond the initial stages were considered.

The Use of Radioactive Inserts in the Study of Metal Deformation During Tube Making Processes. W. H. T. DAVISON, Tube Investments Research Laboratories, Cambridge, U.K.

There is considerable interest in studying the deformations which occur in the hot processing of metals. This paper reports on the use of radioactive inserts in a study of the deformation of steel in hot rotary piercing for tube making.

Iron or steel wires are activated in the pile, inserted in tubes drilled in iron or steel billets, which are then processed under normal production conditions. Careful monitoring shows that the radiation exposures and contamination of the plant are quite negligible.

On cooling, the billets are scanned in the laboratory, using a collimated scintillation counter, mounted normal to the surface of the pierced billet and isodose curves show the shape of the deformed insert normal to the tube surface. A similar scan of a section normal to the axis of the tube gives a second plot; from a combination of the two plots, a three-dimensional picture is obtained.

Some results are quoted, but the main emphasis of the paper is on the experimental technique, which has quite general applicability in metal deformation studies.

The insert must be located within a millimeter or thereabouts, for which a higher resolution is required than is normal in medical scanning techniques. The problems of achieving this are discussed in terms of γ-energy, collimator design and energy discrimination.

The Adsorption of Hydrogen on a Molecular Sieve at −196°, and the Observation of an Isotope Effect. W. G. DUNCOMBE, The Wellcome Research Laboratories, Beckenham, U.K.

Linde Molecular Sieve 4A has been examined as a possible means of handling small volumes of hydrogen isotopes in a vacuum system, as an alternative to the slow Toepler pump method.

The equilibrium pressure (P) was measured for various volumes (V) of hydrogen adsorbed by one gram of Sieve at −196°. A plot of log (P/V) vs. log P was linear over the range P = 0·2 to 8 cm. Experiments with activated charcoal showed the superiority of the Sieve as a hydrogen adsorbent. One gramme of the Sieve in a system of volume 500 ml will adsorb about 97% of a one ml sample of hydrogen. Adsorption is negligible at −78° and desorption is quantitative and rapid at room temperature.

The possibility of an isotope effect was investigated by adsorbing measured volumes of tritium (5 μC/mole) at an equilibrium pressure of about 5 mm, pumping off the system for times up to 15 minutes and measuring the volume of residual hydrogen. The latter was converted quantitatively to water, thence to butane, and gas-counted. The specific activity was always higher than that of tritium which had undergone 10 cycles of adsorption and desorption without intermediate pumping off, so that there was no net loss of gas. This had the same specific activity as untreated tritium from the storage bulb. It was found that log (residual vol./initial vol.) was proportional to 1/log (residual sp. act./initial sp. act.) over the range investigated (0–90% of initial gas pumped off). When 90% had been removed the specific activity ratio was about 3.

Isotopic fractionation during adsorption is possible but in these experiments about 99% of the initial hydrogen was adsorbed on the Molecular Sieve before desorption by pumping off was begun. It seems likely, therefore, that the considerable fractionation observed occurs mainly during desorption. The effect is thus not likely to be important when the Sieve is used for manipulating small volumes of hydrogen isotopes, since complete desorption by warming will usually be employed.

Neutron Activation Analysis of Ancient Silver Coins. M. AITKEN, V. EMELEUS and E. HALL, Research Laboratory for Archaeology and the History of Art, University of Oxford, Oxford, U.K.

The amounts of gold and copper present as impurities in 500 Greek silver coins of the fifth century B.C. have been determined with a gamma-ray spectrometer, following neutron activation. The coinage from eight cities and kingdoms was studied: the average gold content for different groups of coins varies between 0·02% and 0·3%, and the copper content between 0·1% and 10%. Evidence about trading connexions and of deliberate debasements of the coinage has been obtained, and several unsuspected plated coins were detected.

The gold content was determined by measuring the intensity of the 0·411 MeV gamma-ray from Au 198 (2·69 days); for the copper content the 0·511 MeV positron annihilation radiation from Cu^{64} (12·8 hr) was used, and for silver the 0·884 MeV gamma-ray from Ag^{110m} (253 days). Decay measurements were used as a check of identity. The technique of using total gamma-activity decay curves by themselves is insufficiently sensitive. For accurate work the importance is stressed of approximate facsimile standards.

Potentialities of Autoradiography for Comparison of Radioactive Samples. G. W. W. STEVENS and D. SPRACKLEN, Research Laboratory, Kodak Limited, Harrow, U.K.

Quantitative autoradiography of gross specimens has proved useful for evaluating tracer experiments in the photographic industry. This experience suggested that similar methods might be more generally useful in tracer studies. Modified methods of specimen preparation suitable for general chemical work, and methods for assembling many specimens so as to be recorded by a single film are discussed. The remainder of the paper deals with exposing technique, development, film calibration and assessment of results. It is believed that quantitative autoradiography should not only prove a useful alternative to employment of a counter, but in some cases should prove advantageous.

Determination of Hydrogen in Metals by Isotopic Dilution with Tritium. C. EVANS and J. HERRINGTON Atomic Weapon Research Establishment, Aldermaston, U.K.

A method for the determination of hydrogen in metals by isotopic dilution with tritium has been developed. The apparatus and counting technique used are described and results are given for aluminium, beryllium and uranium samples.

The main stock of tritiated hydrogen is stored on pyrophoric uranium, a subsidiary calibrated stock being stored in a glass bulb; precautions are taken to overcome the fractionation occurring during the release from the main stock by mixing thoroughly the gas in the bulb. The exchange reaction takes place on a silica furnace: a diffusion pump is used to remove the gas sample and for circulation of the sample in order to overcome any fractionation which may occur on passing through the palladium tube. The hydrogen-tritium mixture is analysed by counting the latter in a slightly modified glass geiger counter, having a stainless steel cathode. The counter is filled to a pressure of approximately 10 cm with 10% toluene in hydrogen. A second furnace has been used to determine the time and temperature necessary to establish equilibrium between the added tritium-hydrogen and the hydrogen in the metal.

The results obtained by this method are compared with those obtained by other laboratories by vacuum extraction on samples from the same stocks of metals. The vacuum extraction work on the beryllium had indicated that the hydrogen could be entirely accounted for by that adsorbed as water vapour on the surface: the results are quoted as ml/cm².

The total hydrogen and "surface correction" for aluminium and uranium have been obtained by both methods. The values of these quantities obtained by the isotopic dilution method are higher than those obtained by vacuum extraction. However, due to the large "surface correction" there is good agreement for the internally adsorbed hydrogen, which is responsible for the embrittlement of the metals.

The results are summarized below; all volumes are corrected to N.T.P.

Metal	*Isotopic dilution*		*Vacuum extraction*	
Beryllium	$(7{\cdot}5 \pm 0{\cdot}6) \times 10^{-3}$ ml/cm²		$(7{\cdot}0 \pm 0{\cdot}7) \times 10^{-3}$ ml/cm²	
Aluminium	*Dissolved* H_2 ml/100 g	*Surface correction* ml/cm²	*Dissolved* H_2 ml/100 g	*Surface correction* ml/100 g
	0·45	$9{\cdot}4 \times 10^{-4}$	0·37	$1{\cdot}4 \times 10^{-4}$
	$0{\cdot}79 \pm 0{\cdot}05$	$9{\cdot}4 \times 10^{-4}$	0·81	$1{\cdot}4 \times 10^{-4}$
	1·00	$9{\cdot}4 \times 10^{-4}$	0·97	$1{\cdot}4 \times 10^{-4}$
Uranium	$0{\cdot}70 \pm 0{\cdot}02$	$(5{\cdot}46 \pm 0{\cdot}10) \times 10^{-3}$	$0{\cdot}71 \pm 0{\cdot}04$	$3{\cdot}63 \times 10^{-3}$

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The Use of Antimony (124) for Beryllium Analysis. H. Bisby and F. H. Hale, U.K. Atomic Energy Authority, Atomic Energy Research Establishment, Harwell, Didcot, U.K.

Recent advances in the design of nuclear power reactors have lead to a demand for higher working temperatures. The use of beryllium as a canning material for the fuel elements is attractive because it is strong, light, has a low thermal neutron capture cross-section and a high melting point. However, the ordinary chemical or chemical/spectrographic analytical technique used for determining the beryllium content of a sample are complex, slow and expensive. A complete beryllium programme covering field geology, mining, mineral dressing, chemical extraction and purification, metallurgy and medical supervision therefore requires a new analytical technique which ideally should be specific sample, rapid and non-destructive, require little or no sample treatment and be equally applicable to hundred gramme mineral rock samples, ten gramme chemical liquid samples and microgram medical samples.

The specific nuclear property of beryllium (9) whereby it emits neutrons by photodisintegration when irradiated by γ-radiation of energy greater than 1·63 MeV suggested that the exploitation of this (γ, n) reaction could provide an analytical technique to meet most or all of the above requirements. The artificial radioisotope Antimony (124) has the appropriate γ-energy and in any system of fixed geometry, comprising γ-source, beryllium sample and neutron detector, a measurement of the neutrons emitted from the sample is specifically and directly proportional to the quantity of beryllium present by a conversion factor.

The paper deals with the development of a portable (γ, n) electronic equipment which has been used to revolutionize the survey methods of the field geologist and two types of laboratory equipment which can provide a rapid analytical service on almost all aspects of a complete beryllium programme.

Vapour Pressure Determinations on Tritium Labelled Organic Compounds. A. S. Carson, R. Cooper and D. R. Stranks, University of Leeds, Leeds, U.K.

The recent thermochemical interest in organometallic compounds requires the measurement of their latent heats of sublimation. Their vapour pressures are often less than 10^{-6} mm Hg and a radiotracer technique may be used to advantage. The use of a modified Knudren effusion technique, suitable for radioactive solids, lends itself conveniently to such vapour pressure determinations.

The limits of this technique are governed by the specific activity of the labelling isotope within the compound and tritium labelling of organic hydrogen was found to yield very high specific activities. Exposure of the pure inactive compound, in this case tetraphenyl tin, to tritium gas, yielded on purification, a labelled compound with a specific activity high enough to determine a vapour pressure as low as $10^{-10} - 10^{-11}$ mm Hg with accuracy.

The value of this labelling method, in general, is discussed in terms of the irradiation products found during the purification step. The results show that for aromatic compounds the method is capable of producing pure, labelled material of high specific activity without undue radiation damage. This method of labelling could be usefully applied generally to organic compounds containing hydrogen and is convenient in that material can be used "from the bottle", no complex synthesis from active reagents being required, only a rather thorough purification.

The vapour pressure of tetraphenyl tin, isotopically labelled with tritium by the above method, was measured using a modified Knudren effusion technique. An effusion cell in which the hole size can be varied at will is described and tested by theory and experiment yielding a method of evaluating condensation coefficients.

The assay of tritium was undertaken in a windowless flow proportional counter using methane as a counting gas. Characteristics and behaviour of the electronic set-up are described.

The experimental values of the vapour pressures and latent heat of sublimation in the range 20°C–40°C are given.

A New Technique for the Study of Halogen Atom Reactions. G. S. Laurence and D. R. Stranks, University of Leeds, Leeds, U.K.

A new technique has been developed for measuring the rates of gas phase reactions involving halogen atoms. The technique utilizes the effect of the nuclear (n, γ) reaction to generate radioactive atoms which then react with a substrate.

Under certain conditions the atoms formed by the (n, γ) reaction do not undergo hot recoil reactions, but react only as normal thermal atoms. The kinetics of the reactions of the atoms may be evaluated by using a competing reaction whose kinetics are well established. The method depends for its successful application upon the following conditions:

(a) the absence of hot recoil reactions of the atoms following the (n, γ) reaction;
(b) the absence of reactions between the atoms and ions or radicals produced by the gamma rays from the neutron source;

(c) the existence of a suitable competitive reaction which will enable the kinetics of the reaction between the labelled atoms and the substrate to be measured.

When those conditions are fulfilled the technique is very much simpler than photolysis. With a small laboratory neutron source the concentration of the labelled atoms can be made so small that the direct recombination of the labelled halogen atoms can be ignored, so that accurate measurements of the light absorbed and the quantum yield for the production of the atoms are unnecessary, as are a knowledge of the recombination rate, or the use of a sector technique to measure this rate. The method has possible applications to the study of the reactions of halogen atoms with radicals, but this possibility has not so far been explored.

The technique has been developed in the study of the thermal exchange reaction between iodine atoms and methyl iodide.

$$I^{128} + GH_3I \qquad GH_3I^{128} + I.$$

The exchange reaction between iodine atoms and molecules,

$$I^{128} + I_2 \qquad II^{128} + I$$

was used as a competing reaction, and from the rate constant for this exchange, the rate constant and activation energy for the exchange with methyl iodide have been determined, and the values confirmed by direct measurement.

Diffusion Rates in the Region Close to the Free Surface of a Metal. L. W. Barr, D. A. Blackburn and A. F. Brown, Solid State Laboratory, University of Edinburgh, Edinburgh, U.K.

Chemical sectioning methods have been developed whereby sections down to 1 μ in thickness can be removed from the surface of copper single crystals. By these means diffusion coefficients have been obtained using diffusion depths of only 10–15 μ. The accuracy is comparable with that achieved by mechanical sectioning methods using diffusion depths of the order of 1 mm.

Using these techniques the diffusion/temperature curve for antimony in copper has been extended down to 550°C.

Comparison of the results with those obtained by mechanical sectioning shows that the diffusion coefficient obtained from the small diffusion depths at the lower temperatures is significantly lower than that obtained using conventional diffusion depths. Hence it is suggested that the region of a metal near to a free surface is deficient in vacancies.

Diffusion in Moving Grain Boundaries. D. A. Blackburn and A. F. Brown, Solid State Laboratory, University of Edinburgh, Edinburgh, U.K.

Bicrystals of copper have been sheared along the common boundary at rates of 0·3–3·0 μ/hr at temperatures around 725°C. Total relative displacement of the crystals was up to $\frac{1}{2}$ mm. Penetration of Ag^{110} into static boundaries and boundaries moving in this way was studied by autoradiography.

For both moving and static boundaries good agreement is obtained with Fischer's formula: concentration a exp $[-yf(D'/D)]$ where D' and D are the diffusivities in the grain boundary and the bulk crystal respectively and y is the depth below the surface. For the boundaries studied, which corresponded to maximum mis-orientation, $D'/D \sim 10^6$. D'/D appears to increase slightly with total shear and with shear rate but only by a factor of not more than two over the ranges investigated.

The Isotope Dilution Method of Fluorine Microestimation. J. N. Kudahl, J. H. Fremlin and J. L. Hardwick, Department of Physics, University of Birmingham, Birmingham, U.K.

The fluoride ion is adsorbed on glass from acid solution and for solutions containing less than 100 p.p.m. of fluorine the amount adsorbed varies very regularly with concentration.

A certain volume of a carrier free solution of the unstable isotope F^{18} is added to each of a set of acid fluoride solutions which may be a few milligrams, or less, in size. If the solutions are applied to a defined area of glass some of the F^{18} is adsorbed and this can be fixed by raising the pH when equilibrium has been reached. The radioactivity of the glass is a measure of the total amount of fluoride on the glass and can be used to draw an adsorption isotherm from which the fluorine content of an unknown solution in the set can be found. The effects of substances other than fluorine in the material to be analysed will be described in this paper.

The adsorption depends on the pH of the solutions so this must be as constant as possible for the set, although the dependence is not strong in the pH range in which maximum adsorption occurs.

The adsorption process is also modified by the presence of various other ions. Organic material can be burnt off if calcium or magnesium ions are present to prevent loss of fluoride. Precipitation of radioactive fluoride with calcium on the glass when the acid is neutralized can be prevented by increasing the in pH two stages. Phosphate ions affect the adsorption and also alter the pH but these effects can be reduced to a minor correction by using very low concentrations. The accuracy of the method does not depend on the

fluoride concentration down to strengths of a fraction of a p.p.m.

Natural Radioactivity and Meteorology. L. MACHTA, World Meteorological Organization, Geneva, Switzerland

There are many meteorological problems which are especially vulnerable to tracer studies. Some of these can be attacked using nature's own radioactive markings.

Many measurements of radon daughters have been obtained at ground level and related to meteorological conditions. A strong inverse correlation between radon and vertical mixing has often been reported. However, the very few measurements above the ground level such as those at the Argonne National Laboratory on a tower hold promise of much greater meteorological applications.

Similar vertical profiles of radon up to the tropopause offer the possibility of deducing a large-scale atmospheric vertical mixing intensity. In addition, radon may be useful as a tracer of tropospheric air in regions near the tropopause where the thermal structure is ambiguous. The observed increase in Ra-D through and above the tropopause reported by the British should be further studied to clarify the explanation for this unexpected phenomenon.

Cosmic ray-produced radionuclides have received special attention at the Tata Institute in India and at La Jolla. The shorter-lived isotopes such as Be^{7}, S^{35}, P^{32} and P^{33} are especially valuable since they have half-lives of the same time scale as many meteorological processes. Their concentration profiles through the tropopause can complement radon observations since the stratosphere contains much higher concentrations of the cosmic ray-produced radioisotopes than does the troposphere. The ratios of short-lived cosmic ray-produced isotopes have been demonstrated to reflect the residence times of the dust particles to which they are attached. The ratios can also indicate the incursions of recent stratospheric air into the troposphere.

The Radiation Age of Meteorites. K. GOEBEL and P. SCHMIDLIN, European Organization for Nuclear Research, Geneva, Switzerland

Radioisotopes which are produced by cosmic radiation in meteorites while traveling through the space can be used to trace back the history of these bodies. The radioisotopes and the accumulated daughter elements in the meteorite must be determined to evaluate the time during which the meteorite was exposed to the cosmic radiation. (It must be assumed for the calculation that the flux of the cosmic radiation is constant with time). Amongst others, often gas isotopes have been used for these measurements as they can be easily separated from the meteoric substance. In the reported work especially tritium and argon have been used. From the ratio T/He^{3} radiation ages from some few millions to several hundred millions of years have been found. The recent measurements at CERN agree in principle with results of other authors. The probable errors from diffusion losses of gas and the influence of shielding in the preatmospheric meteorite will be discussed in the paper. Taking into consideration the measured cross section for tritium production in the elements which form the meteorite, values of the cosmic ray flux in the outer space can be determined.

Recent Developments in the Application of Radioisotope Techniques in Australia. J. N. GREGORY, Australian Atomic Energy Commission Research Establishment, Lucas Heights, Australia

This paper describes some of the work carried out by the Isotopes Section of the Australian Atomic Energy Commission during the last two years, particularly relating to industrial and field tests in co-operation with other organizations.

A study of the flow pattern of water in a power station cooling pond was the subject of two extensive experiments. A small volume of the warm condenser water was labelled with $iodine^{131}$ as iodide in solution as it entered the pond. The subsequent flow of this water was followed quantitatively throughout the 200,000,000 gallon pond by the use of calibrated underwater scintillation counters. With 500 mc of tracer it was possible to plot the flow pattern until mixing was complete. In one case this took 6–7 days. A recording scintillation detector at the power station pump house measured the rate of return of the labelled water to the power station.

These experiments also showed that the flow pattern was affected by the wind more than by any other factor. A wind opposing the normal hydraulic flow consistently reversed the flow at a quite moderate wind velocity. In the absence of wind an appreciable fraction of the warm water channelled across the surface of the pond and re-entered the power station within 3–4 hours. This indicated a design defect in the layout of the intake which was subsequently modified. The season of the year also had an effect on the flow pattern.

A study of the pattern of flow in a Bach subsider for raw sugar solutions is also described. The hot raw solution after lime treatment enters through a single feed line at the top and clarified solution is taken off by pipelines at six different levels. The solids are taken off at the base. About 5 mc of $bromine^{82}$ in solution was injected into the feed line

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and the appearance of the tracer measured quantitatively by shielded scintillation detectors on each of the six outlet pipes. Analysis of the distribution of activity with time in each line permitted a clear indication of the nature of the flow within the subsider.

Other work described includes the use of phosphorus^{32} labelled lubricants to detect the origin of oil spotting on valuable railway freight and the development of a high precision radiation density gauge for scanning density variations across a slurry pipeline.

Preliminary Experiments on the Use of Radioactive Indicators in Macromolecular Chemistry L. de Brouckère, R. Van Leemput and R. Stein, University of Brussels, Brussels, Belgium

It is well known that osmotic data concerning the second virial coefficient or the molecular weight of high polymers in dilute solutions are of dubious accuracy because of various "membrane effects". These have been the object of intense study in recent years, and it seems to us that important and reliable results might be obtained in this field, by making use of labelled polymers.

Osmotic errors are due mainly to:

(a) diffusion of low molecular weight polymers across the membrane;
(b) polymer absorption on the membrane.

For investigations on both these phenomena radiotracer methods present decisive advantages over the classical and far less sensitive gravimetric procedures.

The polymer used in our experiments was a heterodisperse sample of (poly) chloro-butyl acrylate which was ionically chlorinated with (^{36}Cl) starting from a sample of (poly) butyl acrylate. This polymer was disolved in acetone.

Diffusion chambers similar to twin-cell osmometers were set up.

Cellophane membranes treated to permeabilities of $0{\cdot}5 \cdot 10^{-13}$ to $20 \cdot 10^{-13}$ cm^3 sec g^{-1} separated solution from solvent.

It was found:

(a) that, with our apparatus, about two hundred hours were necessary to reach an equilibrium or steady state in diffusion experiments;
(b) that the fraction of polymer diffusing through the membrane in a given time was independent of the concentration;
(c) that the amount of polymer diffusing was related to the permeability of the membrane;
(d) a practically irreversible adsorption of polymer on the membrane was observed. The amount of polymer fixed per square centimeter of membrane was of the order of 30–40 μg.

Artificial and Natural Radioisotopes in the Antarctic Atmosphere—Some Glaciological and Meteorological Uses. E. Picciotto and S. Wilgain, University of Brussels, Brussels, Belgium

The results of measurements of atmospheric radioactivity during the International Geophysical Year (1958) as part of the programme of the 1957/58 Belgian Antarctic Expedition are briefly described. The measurements in question related to the concentration of fission products and natural radio-elements (radon, thoron, radium D) in the air and in precipitation, and to the intensity of radioactive fall-out.

A description is also given of the distribution of fission products along the 24th meridian East, between 60° North and 70° South.

It is shown that fission products are present in the Antarctic atmosphere and precipitation. Their average concentration in 1958 corresponded to an activity of 3 d.p.m./m^3., i.e. was about 2% of the concentration in the Northern hemisphere. The Ra D concentration in the air was 10^{-16} curies/m^3. These radionuclides can be used for dating the formation of the different sheets of névé and ice during recent decades and for measuring the rates of accumulation on the continent.

The distribution of fission products along a meridian and a knowledge of their average age yield certain data on the meridional exchange of air masses.

The Production of Carrier-free Tantalum by Deuteron Bombardment of Tungsten. A. Demildt and J. Hoste, University of Ghent, Ghent, Belgium

Three different chemical procedures were developed to prepare carrier-free radiotantalum by deuteron bombardment of the natural tungsten element at energies of 12 and 22 MeV. The procedures mainly involve the separation of tantalum from the tungsten bulk material and the simultaneously produced rhenium isotopes.

In the first procedure carrier-free tantalum is adsorbed on iron hydroxide in alkaline medium. Three consecutive adsorptions in the presence of holdback tungsten carrier provide a decontamination factor of better than $5 \cdot 10^5$ from both tungsten and rhenium. The yield of carrier-free tantalum after three steps is about 80%.

The second procedure makes use of ion exchange on Dowex 1-X8 in 0·01M oxalic acid + 2M HCl, after scavenging the tantalum with iron hydroxide. The distribution constants of Ta, W and Re in this medium are respectively 5·5, 62·7 and 399 so that a quantitative separation is possible. This method offers the advantage of separating radiotantalum from radioniobium, which is formed if traces molybdenum

are present in the tungsten target. The overall yield of carrier-free tantalum is approximately 50%.

Carrier-free separation of tantalum is finally possible by liquid–liquid extraction from a hydrochloric-hydrofluoric acid solution using either diisopropyl- or diisobutylketone. The former proves to be superior as the distribution constants of tantalum, tungsten and rhenium are respectively 203, 0·15 and 0·8 against respectively 16, 0·065 and 0·075 for the latter. In this procedure rhenium is removed by volatilization in perchloric acid, prior to the liquid–liquid extraction. Recovery of tantalum is respectively 60% and 50%.

The analysis of the decay curves, of the gamma spectra and of the Feather absorption curves shows that 2 tantalum isotopes are formed at a deuteron energy of 12 MeV, namely Ta^{184} and Ta^{182} by (d, α)-reactions on W^{186} and W^{184}. Besides Ta^{183} is formed at a deuteron energy of 22 MeV by a $(d, \alpha n)$ reaction on W^{186}.

The thick-target yields of Ta^{184} and Ta^{182} at a deuteron energy of 12 MeV correspond to 0·4 μC/μAh and $1{\cdot}3 \times 10^{-3}$ μC/μAh resp. At 22 MeV these yields are resp. 0·85 μC/μAh and $2{\cdot}7 \times 10^{-3}$ μC/μAh, whereas the yield of Ta^{183} is 0·23 μC/μAh.

A Francium-223 Reservoir Source. J. Fouarge and W. W. Meinke, University of Liège, Liège, Belgium

By improving and accelerating a method which had been earlier tried for caesium-rubidium separation on a cellulose column, i.e. elution with 2N HCl-equilibrated phenol, we succeeded in obtaining consecutive and quasi-selective elutions of FR-223 starting with actinium-227 fixed at the top of a small cellulose column to which ZrO_2 had been added.

The francium-233, rapidly eluted under pressure, is extracted by water while the phenol is extracted by ether; it can easily be cleared of any residual traces of radioactive contaminants (Tl-207, Ra-233, Th-227) by two consecutive $BaSO_4$ precipitations. The preparation of a Fe-223 solution (HCl-H_2SO_4) requires approximately 20 minutes; the time noted for Fr-223 was closer to 22 than to 21 minutes.

Production of C-14 Labelled Compounds from CO_2-14 Accelerated in an Electric Field. Physicochemical Analysis of the Radioactive Compounds Obtained. M. Guillaume, University of Liège, Liège, Belgium

This method of labelling which is based on the acceleration onto a target consisting of a thin layer of organic substance, of CO_2-14 ionized by an electric field, constitutes a quick and effective means of introducing a C-14 activity of as much as 200 μC/g into certain types of organic structure.

The apparatus consists of a filling cell with a volume of 125 cm³, fitted with two silver or noble metal electrodes. After introduction of CO_2-14 of specific activity 24 mC per mmole at a pressure slightly less than $5 \cdot 10^{-2}$ mm Hg, a steady difference of potential of a few hundred volts is applied during a period which varies from 2 to 10 hours according to the activity desired, the degree of stability of the bombarded molecule and the yield of the operation. The organic compound dissolved in a suitable solvent undergoes a series of extremely thorough purification processes. Even so, an appreciable quantity of elementary C-14 contaminates the parent product, and this must be eliminated as far as possible. Chromatographic techniques are particularly suitable for this type of purification.

The qualitative results obtained clearly show that, with this labelling method, aliphatic substances are much more sensitive than aromatic molecules which, in certain cases, cannot be labelled.

Tritium Counting in the Geiger Region. R. Coekelbergs, A. Frennet and G. Liénard, Institut interuniversitaire des sciences nucléaires, Brussels, Belgium

During the exchange study we encountered the need to perfect a method of counting tritium in the form of a gaseous halogenated organic derivative. Special attention was paid to the design of a self-quenching counter operating in the Geiger region for measuring the radiochemical concentration of tritium in methyl chloride.

The effect of the nature and of the partial pressure of certain rare gases was determined. The effect of variation in the partial pressure of the methyl chloride was also ascertained. Finally, it was shown that the presence of small quantities of chlorine considerably increases the length of the plateau.

The most interesting features discovered were:

(a) a threshold at about 1 200 V
(b) a plateau between 1 400 and 2 700 V
(c) a slope of less than 2% per 100 V
(d) a dead time of the order of 100 μsec.

There was no sign of any memory effect when using a stainless steel cathode.

Use of Carbon-14 for Studying Elementary Carbon Exchange Between Methane and its Chemisorption Residues on Metallic Films. R. Coekelbergs, J. Decot, A. Frennet and G. Liénard, Institut interuniversitaire des sciences nucléaires, Brussels, Belgium

Various methods are employed in the study of heterogeneous reactions involving hydrocarbons.

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By measurement of chemisorption it is possible substantially to determine the statistical composition of the surface radicals formed and to identify phenomena such as carburation, etc.

Displacement of these surface radicals makes it possible to determine their nature.

Studying the kinetics of exchange between two gases on contact with a catalyst indicates a reaction picture implying the existence of certain surface radicals. These are generally considered to be in adsorption description equilibrium with the gaseous phase. We showed, however, in the course of our study of radiohalogen exchanges, that the catalyst is not the metal surface only but actually an adsorbed radical in exchange equilibrium with each of the two gases. This mechanism makes it possible to identify the two "elementary" stages of the "total" exchange. We have recently been studying the reactions of methane on molybdenum films. Chemisorption and displacement with hydrochloric acid of the surface obtained were the subject of a publication which has already appeared. Various authors have also studied total exchanges between CH_4 and D_2 and also between CH_4 and CD_4 on metallic films.

To verify the application of the "elementary" stages mechanism to the particular case of methane, we used C-14 to study carbon exchange between methane and its chemisorption residues on molybdenum film. The surface was marked in two ways: by chemisorption of $C14H_4$ at different temperatures; or by exchange between $C14H_4$ with a high specific activity (one curie per mole) and a metallic film previously treated with inert methane. The C-14 is counted in the form of CO_2 in the Geiger region.

The results show that the rate of exchange can be measured from approximately 100°C onwards, and that it reaches a maximum at about 250°C. Furthermore, the exchange is governed by laws which vary according to the prior thermal treatment of the surface.

The radioisotopes method is particularly valuable for study of these "elementary" stages involving the determination of a complete kinetic law with reference to quantities not exceeding 10^{18} atoms.

Progress Towards a Phosphorus-33 Production: Studies on the Enrichment of Sulphur-33 by Means of Anion Exchangers. S. Forberg and T. Westermark, Kungl. Tekniska Högskolan, Stockholm, Sweden

Some research opportunities opened by a second radiophosphorus isotope P^{33} (in addition to the common P^{32}), are shortly summarized.

Enrichment of S^{33} by chemical exchange between HSO_3^- and H_2SO_3 was selected as the most promising mean for P^{33} production. HCl displacement of HSO_3^- from anion exchangers was found to be a very convenient method for obtaining counter-current and bulk reflux conditions for this system. Some inherent drawbacks concerning the very high reflux requirements are pointed out.

In this institute a plant has been constructed for this process, and the obtained parameters, operation experiences and results are presented.

For economical reasons the enriched S^{33} must be irradiated in high-flux reactors with corresponding requirements on the thermal stability of the target. Also, the sulphur must be quantitatively recovered without isotope dilution after separation of the induced phosphorus activities. $MgSO_4$ has been selected as a suitable chemical form of the target sulphur. The method developed for separation of the radiophosphorus is described.

In addition to a P^{33} production, the separation of sulphur isotopes may result in three other ways of contribution to the physical sciences, which are shortly reviewed as follows:

(1) The quadrupole moment of the S^{33} nucleus and the absence of n.m.r. amongst the other stable sulphur isotopes might render enriched S^{33} as a unique tool for certain structural investigations of sulphur compounds.

(2) Besides S^{33} the isotope S^{34} is enriched at a much higher rate. S^{34} can be used as an inactive tracer or for double labelling with S^{35}.

(3) S^{36} is enriched in small quantities and, with S^{36} as target, studies are planned for preparation and characterization of P^{35}, P^{36} and Si^{33}.

Activation Analysis by Means of Coincidence Spectrometry. K. Ljunggren, Kungl. Tekniska Högskolan, Stockholm, Sweden

In activation analysis the element sought is determined from the irradiated sample by radioactivity measurement relative to a standard. In the majority of cases, especially when high sensitivity is required, this necessitates a complete chemical separation of the sample to permit the selective activity measurement to be made. In certain favourable cases, scintillation or proportional spectrometry of γ- and X-radiations can furnish the required measuring selectivity without any manipulations of the sample or after rather simple separations into different element groups.

When the rejection ratio of sample background to signal is not sufficiently large, this being rapidly encountered when the nuclide to be determined and the dominating background constituent have similar spectral γ-ray distribution, coincidence techniques may be used to extend the range of accessible concentrations for nuclides which are γ-ray cascade or positron emitters.

A post-coincidence energy-selective spectrometer with sodium iodide scintillators operating at a resolving time of 25 mμ sec has been used for measurements of certain nuclides fulfilling this condition in typical backgrounds encountered in practical activation analysis problems. Results on sensitivity and rejection ratios will be given.

A method has been devised where measurements at different resolving times are used to obtain quantitatively both or all three components in binary or ternary mixtures respectively of nuclides, one of which is a cascade γ-radiation or positron emitter.

The Use of Radioisotopes for Determination of Complex Equilibria. J. RYDBERG, Försvarets Furskningsanstalt, Stockholm, Sweden

Radioisotopes can be used for determination of complex equilibria in solution, provided this solution is in equilibrium with another phase. The most versatile systems for studying aqueous solutions uses solvent extraction and ion exchange methods. In fact, these two methods are more universally practical for determination of complex equilibria than e.m.f, spectrophotometric and other more conventional ones. The practical steps of these two methods are discussed in the following order: (1) basic equations, (2) experimental methods, (3) principles of solving the equations, (4) uncertainties in the constants obtained.

Use of Radioisotopes in the Systematic Analysis of Impurities in Metals of Very High Purity. P. ALBERT and J. GAITTET, Metallurgical Chemistry Research Centre, Laboratoire de Vitry, Centre national de la recherche scientifique, Vitry, France

Using the "zone melting" method, very high purity metals with impurity concentrations of the order of 10^{-6} to 10^{-8} can be obtained. These metals are prepared in small quantities only and it must be possible to determine, with great sensitivity the content of a very large number of elements from a single sample.

In Professor G. Chaudron's laboratory at Vitry we developed a method for systematic analysis of aluminium and iron after neutron irradiation. The main importance of this method is that, with it, 45 elements can be determined from a single sample of the order of 1 gramme. This analysis of a large number of impurities was made possible only by the cascade separation of radioisotopes created during irradiation in more than 40 analytical fractions. Most of the radioisotopes are then isolated radiochemically pure and are simultaneously identified by study of their radioactivity decay period and γ-ray spectrum.

Irradiation was usually carried out in fluxes of approximately $10^{12}n/cm^2/sec$ (EL_2 at Saclay), under which conditions the quantity determination sensitivity was at least 0·1 p.,p.m. (10^{-7}) and frequently attained 0·001 p.p.m. (10^{-9}).

Application of this method of systematic analysis to the study of aluminium and iron purification by the "zone melting" method made it possible to demonstrate the high purity of the metals obtained. It also showed the extremely important role which very low concentrations of certain impurities can play.

While systematic analysis permits the determination of 45 elements, it may, however, be anticipated that some 60 elements may be determined by the irradiation method, and for various reasons, e.g. too brief a decay period, requirement of too special chemical separation, or too slight a probability of reaction with the neutrons, we decided to determine certain elements from separate samples either by neutron irradiating (in the case of sulphur, phosphorus, chlorine, barium etc), or by recourse to the reactions produced by the deuterons (in that of carbon and boron).

We intend to lay special emphasis in the paper on the results and implications of our analyses.

Use of Radioisotopes in Studying the Penetration of Sulphur into Iron During Hydrogen Cathode Charging. S. BESNARD and J. TALBOT, Metallurgical Chemistry Research Centre, Laboratoire de Vitry, Centre national de la recherche scientifique, Vitry, France

Certain elements, such as arsenic for example, are commonly used in the laboratory to facilitate the penetration of hydrogen into iron. It has been found in industry that steel corrosion caused by hydrogen was aggravated by the presence of sulphuretted hydrogen.

It was an interesting question whether these elements, hitherto considered to be catalysts, merely permitted a higher hydrogen absorption or whether, on the other hand, they directly affected the metal.

A study of this phenomenon was undertaken in our laboratory, using electrolytic pure iron. Hydrogen supersaturation was effected by cathode charging. The addition element was sulphur-35 labelled sodium sulphide.

We were able to show that, in half an hour, at −15°C, the sulphur penetrates into the iron to a depth of some 120 μ. A preferential localization of the sulphur at the grain boundaries was also noted. This result, which could not have been obtained without the help of radioactive tracers, has important consequences, especially for the oil industry.

A similar study was made using phosphorus-32.

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Special Synthesis of Certain Iodized Organic Compounds. R. HENRY, E. JUNOD and D. DEBUCHY, Commissariat à l'énergie atomique, Centre d'études nucléaires de Saclay, France

The technological difficulties of working with radioactive products call for maximum simplicity in methods of chemical synthesis.

For iodized compounds we selected two special methods:

(a) Utilizing fission recoil, simple iodized compounds, such as iodobenzene or methyl iodide were prepared with good yields and a good degree of purity.
The method consisted or irradiating mixtures of uranium oxide and benzoic acid or ammonium acetate. The iodized product was separated by distillation after dissolution of the recoil medium in a solvent.

(b) By isotopic exchange between mineral iodine with different valencies and complex molecules such as rose bengale and diodene, satisfactory labelling yields were also obtained. These reactions were arranged so as to reduce the isotopic exchange time to the minimum.
For rose bengale a yield of 90% after 60 minutes was obtained by exchange between NaI and the organic molecule in an aqueous medium and in the presence of oxygenated water.
For diodone the method proposed by Liebster was adapted to reduce losses during purification.
A description of the methods of analysis chosen for these different compounds is also given.

Use of Radioactive Sources for Studying Wear of Refractory Linings. G. COURTOIS, R. HOURS, P. LE CLERC and A. PONS, Commissariat à l'énergie atomique, Centre d'études nucléaires de Saclay, France

Determining the degree of wear of refractory materials is a problem to which the solutions so far found have been few in number, limited in scope or difficult to apply.

For this reason, the success achieved in the use of radioactive tracers bedded in the refractory substance has been widely welcomed. Unfortunately, development of the method has been hampered by the fact that the amount of radioisotope incorporated in the metal products must be strictly limited, and also by the diffusion of the radioactive substance in the refractory material which has been noted.

As a consequence, the maximum content permitted in France is now 1 mc/500 metric tons of cast metal, and no individual source may exceed 3 mc. We have developed sources especially designed to avoid diffusion phenomena. The essential feature here is the use of pyrocerame, a non-porous material, with a high fusion point, and great chemical inertness. In these sources the radioisotope can be completely enclosed in the pyrocerame or it can form an integral part of its composition. A comparative study of the two types of source is at present in progress.

Self-diffusion in Volume and at the Grain Boundaries of Gamma-iron of High Purity (99·99). P. LACOMBE, P. GUIRALDENQ and C. LEYMONIE, Ecole nationale supérieure des mines, Paris, France

In view of the difficulty of measuring accurately self-diffusion coefficients, whether in the mass or at grain boundaries, within a given temperature range in which the two phenomena co-exist, we decided to reconsider the classical cutting method.

We established that, in the case of a semi-infinite solid, the post-diffusion concentration $C(X_n)$ of radioactive atoms at distance X_n from the initial radioactive deposit is a simple function of the over-all activity remaining in the sample after abrasion to depth X_n. This conclusion was reached as a result of the general application of the GRUZIN formula (*Dokl. Akad. Nauk SSSR* **86,** 289 (1952)) which up to now had been applied only to diffusion in volume. We have shown that, by measuring the remaining overall activity as a function of the depth of penetration, we could distinguish the part of the activity due to self-diffusion in volume from that due to intergranular self-diffusion. The advantage of this method is, therefore, that it enables us to follow continuously on the same sample the passage from self-diffusion in volume to intergranular self-diffusion.

We used this new method for measuring the self-diffusion constants in gamma iron in volume between 1260° and 918°C and at grain boundaries between 1020° and 918°C.

The activation energy values in volume and at the grain boundaries are $Q_v = 59$ Kcal/At g and $Q_j = 39$ Kcal/At g.

The frequency factors are:

$$D_v^0 = 3{\cdot}7 \times 10^{-2} \text{ cm}^2 \text{ sec}^{-1}$$

$$D_j^0 = 1{\cdot}4 \text{ cm}^2 \text{ sec}^{-1}.$$

The D^0 at the grain boundaries has been calculated by means of the Fischer formula, which assumes that the width of the grain boundaries is constant. In spite of the reservations which might be made in respect of the hypothesis, we have assumed that the width in question is equal to 5 Å.

Measurement of the C/H Ratio by Neutrons. P. MARTINELLI and M. HUARINGA RICCI, Commissariat à l'énergie atomique, Centre d'études nucléaires de Saclay, France

A probe consisting of a Ra (α, n)Be neutron source and a boron trifluoride filled proportional counter was used for measuring the C/H ratio in hydrocarbons.

The intensity of the thermal neutron flux near the counter increases in proportion to the increase of the hydrogen concentration in the hydrocarbon surrounding the probe. The C/H ratio can be deduced by measuring the density.

The C/H ratio can be estimated as accurately by this method as by β-particle transmission. The errors resulting from the chemical nature of the hydrocarbon can be reduced to the minimum.

The advantage of using this method is that it makes possible the measurement of the C/H ratio of hydrocarbons contained in steel vessels or thick steel channels by means of a portable external apparatus.

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Examples of the Use of Preparatory Gas Chromatography in the Manufacture of Labelled Molecules. L. PICHAT, C. BARET, J.-P. GEURMONT et M. AUDINOT, Commissariat à l'énergie atomique, Centre d'études nucléaires de Saclay, France

Gas chromatography is most widely used in the analysis of volatile products. Certain works mention its use for preparatory purposes.

Organic labelled molecule preparations are usually made in respect of quantities of the order of 1–10 mmole. It has thus been possible to use gas chromatography with very little alteration for the purification of C-14 labelled molecules and their separation from complex reaction mixtures.

The apparatus employed may be briefly described as follows: The chromatography columns used (diameter: 9–12 mm, length: approximately 4–6 m) made it possible to separate labelled products with boiling-points of up to 180°C and in quantities of approximately 100 mg to 1 g. The fractions detected by a conventional conductivity cell device were condensed in traps cooled by liquid nitrogen. The radioactivity was not measured at the same time, as an ionization chamber capable of operating at up to 100°C is still only at the research stage. In all cases, the vector gas was helium and the stationary phase support was usually 80 mesh "celite 545".

The *acetone*-2-C^{14} produced by pyrolysis of barium acetate was purified on a "polyglycol 200" column. The water and any unidentified impurities are readily eliminated.

The *benzene* C_6^{14} produced by cyclizing polymerization of the acetylene-C^{14} in acetonitryl was quantitatively separated from the complex reaction mixture on a nonyl phthalate column at 80°C.

The *methyl or ethyl acrylates* formed, according to Reppe, by the action of radioactive acetylene on a mixture of methanol or ethanol, water and hydrochloric acid, in the presence of nickel carbonyl, are difficult to separate by distillation in small quantities. Two columns were used in series: one consisted of a "Linde 5 A" molecular sieve having a triple purpose: fixation of the water, fixation of the methanol and neutralization of the hydrochloric acid; the second column composed of nonyl phthalate brought about separation of the ethyl or methyl acrylate from the nickel carbonyl.

The p-*cymene*-7-C^{14} obtained by reducing the cuminic acid labelled with C-14 in the carboxyl group with a mixture of $LiAlH_4$ and $AlCl_3$ is contaminated by cuminic alcohol-7-C^{14} which cannot be separated by distillation in microquantities. Gas chromatography on a silicone column at 125°C made it possible to obtain pure *p*-cymene.

A Simple Method for Preparing Be-7 by Spallation on Water. R. BERNAS, GRADSZTAJN, Nuclear physics laboratory, Faculté des sciences, Orsay, France

Very pure Be-7 sources can be obtained without chemical separation by irradiating water with high-energy protons. The 155 MeV proton beam of the Orsay Laboratory synchro-cyclotron was used for this purpose. Details will be given of the values of the formation cross-sections for different energies and of the purity of the sources obtained.

A New Method for the Preparation by Biological Means of Certain Sulphurated Substances Labelled With S-35. F. CHAPEVILLE, H. MAIER-HUSER and P. FROMAGEOT, Commissariat à l'énergie atomique, Centre d'études nucléaires de Saclay, France

Previous investigations have shown that the yolk-sac of embryonic birds' eggs can be used to produce the following reactions:

(a) reduction of sulphate to sulphite
(b) fixation of sulphite on the carbon chain produced by the desulfhydration of L-cysteine, with formation of L-cysteic acid.
(c) decarboxylation of the L-cysteic acid into taurine.

The enzymatic system which causes reaction (b) has been purified. It also acts as a catalyst in the sulphur exchange between the cysteine and the mineral sulphide.

These data can be used for preparation of S-35 labelled L-cystine, S-35 labelled L(+)cysteic acid and S-35 labelled taurine. In fact, if L-cysteine and S-35 labelled sulphide are incubated in nitrogen at

pH 9 and 38°C, in the presence of a protein function isolated from the yolk-sac and the yolk of embryonic birds' eggs, the following enzymatic exchange is brought about:

$$SH—CH_2—\underset{NH_2}{CH}—COOH + S^{35}H^- \rightleftarrows H^{35}S—CH_2—\underset{NH_2}{CH}—COOH$$

Over a period of 24 hours the yield is 70 to 80% of the theoretical amount. The S-35 labelled L(−)cysteine obtained is isolated in the form of L(−)cystine.

The same protein fraction acts as a catalyst in the synthesis of S-35 labelled L(+)cysteic acid from S-35 labelled sulphite and L(−)cysteine:

$$S^{35}O_3H^- + SH—CH_2—\underset{NH_2}{CH}—COOH \rightarrow SH^- + S^{-35}O_3^-—CH_2—\underset{NH_2}{CH}—COOH$$

In this case, the optimum pH is 8·5 and the yield is in the order of 70 to 80%.

The synthesis of S-35 labelled L(+)cysteic acid can be linked with that of S-35 labelled taurine. In this case, yolk-sacs and S-35 labelled sulphate are incubated for 15 hours in the air without carrier.

By then 30 to 35% of the S-35 labelled sulphate introduced is in the form of S-35 labelled taurine and S-35 labelled L(+)cysteic acid, in the proportion of approximately 9:1. After the addition of taurine and L(+)cysteic acid as carrier, one of these substances is isolated—its specific activity can thus be approximately selected.

Statistical β-Ray Voltmeter. R. VINET, F. BARRAULT and A. DELPOUY, Electricité de France, Direction des Etudes et Recherches, Paris, France

This voltmeter is based on the principle of impression of a fixed photographic film by a radioactive source mounted on its pointer. Since the blackening at one point of the film, depending on the choice of the latter, is proportional to the time during which the pointer remains facing this point, it is possible to establish, directly after scanning of the film by a microphotometer, the time distribution curve, which is substantially Gaussian, of the voltage employed.

The use of a radioactive source with an intensity of only a few microcuries, instead of an orthodox luminous source, considerably simplifies the apparatus and greatly facilitates introduction and removal of films, which can then be used with their usual protection against light.

The use of such voltmeters in electricity networks makes accurate measurement of the voltage stability possible and hence the ascertainment of any improvements necessary to ensure the most satisfactory service.

The variations in the voltage applied to the voltmeter may of course reflect random variations of any magnitude. This principle can be used more generally for determining the time distribution curve of any variable phenomenon which can be related to the movement of a pointer.

Strontium-90 provides good results. This radioisotope, used in its insoluble form and at very low activity (maximum 20 μC), is enclosed in the centre of a plexiglass sphere of 23 mm diameter having high mechanical strength. The sphere is fixed on the axis of the voltmeter assembly, and the radiation is emitted through a small plexiglass tube flattened at its end in front of the film.

Solid Sources of Krypton-85. J. PUIG and J. SANDIER, Commissariat à l'énergie atomique, Centre d'études nucléaires de Saclay, France

Krypton-85. a beta emitter with a long half-life and low biological hazard, can be used with great advantage for industrial purposes.

It is difficult, however, to produce Kr-85 sources for industrial use, since this element occurs in gaseous form and cannot be chemically fixed. It must, therefore, be fixed by physical means, either in the compressed gas state, which involves intricate problems of confinement, or in other condensed forms, such as organic clathrates. The latter may, however, be altered by physical and chemical agents.

In our paper we describe a method of krypton fixation in a solid macromolecular matrix and some sources produced by this method.

The characteristic feature of the method is formation of the macro-molecular matrix by mass polymerization of a liquid monomer containing the krypton. The latter can be simply dissolved in the monomer or adsorbed on a finely divided microporous carrier which is suspended in the monomer.

Sources with a specific activity close to 0·1 c/g have been produced by this method using vinyl acetate. The krypton used contained 3% of krypton-85, which was adsorbed on a powdered molecular sieve at −30°C. The polymerization of the vinyl acetate containing the molecular sieve suspension was carried out at −30°C.

The activity of the sources was studied over a period of time at 20°C. An apparent half-life of approximately one month was established.

One of these sources was grafted with styrolene and the apparent half-life was thereby increased by 30%.

At 75°C vinyl polyacetate sources have an apparent half-life ten times shorter than at 20°C.

The sources produced so far by the proposed method quickly lose their activity. This major fault, which is due to the permeability of vinyl polyacetate by gases, could be corrected by choosing more suitable polymers. The advantages of such sources would be their stability with respect to chemical and physical agents and their ease of manufacture.

Study of Pentane and Cyclopentane Radiolysis with the Aid of Radioactive Iodine. J. DAUPHIN, Laboratoire de chimie physique, Paris, France

Irradiation of carbon by ionizing radiation such as Co-60 gamma rays produces, *inter alia*, free radicals. Analysis of these radicals may lead to at least a partial explanation of the phenomena occurring.

A current method of locating these radicals consists of associating them with iodine so as to produce organic iodides which can be analysed,

$$R + I_2 \rightarrow RI + I.$$

Since the transformation rates must remain very low in order to avoid secondary phenomena, it follows that the iodides formed are highly diluted (10^{-4} M to 10^{-3} M).

For analysis, the "isotopic dilution" method is used: the iodine used for taking up the radicals is labelled with iodine-131, resulting in a whole series of labelled iodides when the reaction is completed. Separation is affected by means of distillation on a microcolumn after inactive carriers have been added and the mineral iodine has been extracted. The activity of each fraction is measured directly it leaves the column. A control is used to obtain absolute G values from the counting.

Precautions are taken to prevent isotopic exchange during separation.

This method has been applied to cyclopentane and *n*-pentane and has yielded a detailed radiolysis spectrum.

Radioactive Thickness Gauge. J. GUIZERIX, Commissariat à l'énergie atomique, Centre d'études nucléaires de Grenoble, France

The author describes a thickness gauge in which the scintillating crystal detector alternately "sees" a radioactive source through the material which is to be measured and then a control source of the same material; the radiations are separated in time by an absorbing valve whose sections are alternately full and hollow.

The currents corresponding to the two sources are separated beyond the photomultiplier tube by a detector synchronized with the rotation of the valve.

The quotient of these two currents is then obtained with a standard recording potentiometer. The result is found to be that the average value of the response—which is in the form $G = f(I_1/I_2)$—is not affected by decay of the radioactive sources, and that it is little influenced by variations of high tension, temperature, or properties of the air in the source-detector interval.

Performances of the gauge are given for various radioactive sources.

New Developments in the Analysis and Measurement of Thicknesses by β-Particle Excitation of X Fluorescent Rays. P. MARTINELLI and G. SEIBEL, Commissariat à l'énergie atomique, Centre d'études nucléaires de Saclay, France

The method of analysis and measurement of the thickness of deposits by β-X fluorescence which we previously described has been further developed.

Using promethium-147 and krypton-85 sources, it is possible to reduce the background observed with strontium-90. We quote the results obtained for various thickness measurements of metal deposits, an analysis of the solutions, and the continuous measurement of calcium and iron in core samples.

We describe experiments made for analysis of the X-radiation by crystal.

The results obtained when a double excitation is produced by using an interchangeable primary target are also described.

Use of Alpha Radiation for the Industrial Measurement of Surface Weight. J. PERETTE and J. MAUGEST, Compagnie d'applications et recherches atomiques, Saint Denis, France

The possibility of using alpha radiation for industrial measurement of the surface weight of thin materials has been mentioned by several authors. The techniques have been adapted for industrial use thanks to research on new equipment which, while employing standard techniques, were specially designed to use alpha radiation.

To compensate for variations in the absorbent capacity of the source-detector interval, a two-path differential method must be used. By alternate feeding of the ionization chambers, alternate amplification and detection circuits can be used without prior conversion of the ionization current. The measurement range extends from 6 to 55 gms/m² and

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is accurate to 1% in conditions of perfect stability. The complete equipment used for continuous measurement on production machines is described. The technique can also be used with beta radiation.

Use of Radioactive Tracers in Studying the Transport of Solids in Watercourses. P. JAFFRY and M. HEUZEL, Electricité de France, Laboratoire national d'hydraulique, Chatou, France

The National Hydraulics Laboratory which, in collaboration with the Saclay Nuclear Study Centre, has for several years been devising equipment and techniques for the study of sediment movements by the radioactive tracer method, is now endeavouring to develop a really quantitative method of research.

Two river experiments were recently made, the first a study of shingle drifting in the Rhône, the second a study of sand movement in the Niger.

The latter experiment was matched by identical experiments carried out on a scale model of the River Niger which the Chatou Laboratory has at its disposal. The experiments used Mn-56 radiation obtained by direct activation of crushed apricot stone, this representing in the scale model the natural sediment of the Niger bed.

The Chatou Laboratory and the Saclay Nuclear Study Centre are at present both devoting attention to the application of radioactive tracers in studies with scale models, with the double object:

(a) of obtaining a single research tool for use under natural conditions and with scale models in order to gauge the trustworthiness of the model, in the calibration testing stage;
(b) of taking advantage of the facilities for direct observation and measurement offered by scale models in order to study prospects of improving the tracer method—particularly with regard to obtaining quantitative data.

Determination of the Humidity of Wool by Neutron Scattering. J. A. JANIK, A. SZKATULA, S. WRONKA, E. KUNISZ, Zaklad Fizyki Jadra Atomowego, Polska Akademia Nauk, Cracow, Poland

Based on a previously developed method for the determination of soil humidity by the measurement of neutron scattering, an attempt has been made to apply this technique to the determination of the humidity of wool.

In spite of a large hydrogen content in the structure of wool, it is possible to measure the humidity in the range 0% to about 20%. Measurements were performed with a Po–Be neutron source and a boron trifluoride proportional counter enriched in B^{10}.

Investigations on Structure of Complex Compounds by Radioisotope Exchange. Structure of Cyanonitrosyl Complexes. B. JEZOWSKA-TRZEBIATOWSKA, J. ZIOLKOWSKI, University of Wroclaw, Wroclaw, Poland

The nitrosyl group as the complex ligand is of particular interest because of its structure as well as its ability to form NO^- or NO^+ groups. In the case of co-ordination of NO^+, the valency of the metallic ion in the complex is lowered by a factor of two. To study the electronic structure of $K_3Mn(CN)_6$ and $K_3Mn(CN)_5NO$, the valency of the metal and the bonding type, investigations have been carried out applying the method of radioisotopic exchange, as well as other physico-chemical methods. It has been found that by introducing the nitrosyl group into the hexacyanate ion the stability of the complex is largely enhanced both in the solid state and solution. This observation was confirmed by investigation of exchange kinetics in the systems:

$$\text{I} \qquad K_3Mn(CN)_6 + KC^{14}N$$

$$\text{II} \qquad K_3Mn(CN)_5NO + KC^{14}N.$$

In both cases, the exchange reactions are of first order, taken as function of time, but differ considerably in their velocities: $R_0^{\text{I}}o = 5{\cdot}1 \cdot 10^{-4}$, $R_{18}^{\text{II}}o = 2{\cdot}77 \cdot 10^{-6}$ mol/l. min. The activation energies of this process are $E_{\text{I}} = 8{\cdot}5$ kcal/mol and $E_{\text{II}} = 22{\cdot}8$ kcal/mol. The anion $Mn(CN)_5NO_3$ is sensitive to light, so that the exchange reaction is photochemical in character. The ratio of the exchange velocity constants in the dark and at standardized illumination is 1:100. The first exchange reaction (I) proceeds according to the association mechanism while the second one (II) possesses a composite association-dissociation mechanism. Analysis of the partition of activity within the cyanide groups undergoing exchange in the isotopic equilibrium state, revealed the identity of at least four cyanide groups. The high stability of the nitrosyl complex as compared with the hexacyanate was proved by spectrophotometric and electric conductivity methods as well as lack of secondary dissociation. The central atom in the nitrosyl complex does not undergo either polarographic reduction or oxidation. $K_3Mn(CN)_6$ is paramagnetic (3·4 B.M.) while $K_3Mn(CN)_5NO$ is diamagnetic in the solid state as well as in solution. Cryoscopic determination of molecular weight in fused Glauber's salt excluded binuclearity as the origin of diamagnetism. Characteristic results have been obtained by examination of the absorption spectrum of the complexes. Both the bands are similar within visible range for $K_3Mn(CN)_6$ at 475 m and for $K_3Mn(CN)_5NO$ at 540 m which

corresponds to bands always appearing in the absorption spectra of Mn(III). On the basis of the investigations carried out, it has been found that, by introducing the nitrosyl group into the cyanide complex, the change in electronic structure results in increased stability in optical characteristics (the band peculiar to Mn III). This behaviour points to a NO^- structure in the complex. Previous research has shown that the nitrosyl group is co-ordinated as NO^+. This suggests a resonance structure of the complex by assuming the resonance of an electronic pair between the T_{2g} shell of the central atom and the p shell of the nitrogen atom.

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Gamma Radiography of the Bronze Door of the Royal Cathedral at Gniezno. Z. GODLEWSKI, Polska Akademia Nauk, Warsaw, Poland

A knowledge of the technology of historical objects is important for the knowledge of history of technique. There is in Poland a very interesting object: the door of the cathedral at Gniezno, cast in bronze in the XIIth century. This door is composed of two wings which are different as to the character of bas-relief, the dimensions, and the technology. The dimensions of the left wing are: 3280 mm high and 840 mm wide, and of the right wing are: 3230 mm high and 830 mm wide. On every wing on the front side there are nine quarters with sculptured figures. All the scenes are surrounded on every wing by an ornamental belt environed on its turn by ledges.

An investigation of the medieval technology of such a great casting was interesting both from the point of view of the history of arts and the history of casting. In this case the matter was to confirm: whether the cast had been made in the whole or in parts and also how the liquid metal had been carried to the casting mould. In addition, radiologists were interested in the degree to which radiographic investigations can solve such problems.

Already in 1954, on the basis of exact external examination and partial radiographic investigations using X-rays, it was confirmed that the right wing of the door is composed of some parts cast separately and bound together by means of hard soldering. These investigations did not decide, however, the manner of construction of the left wing, the quantity of parts composing each leaf and the way in which these parts were cast. X-radiographs did not give the complete picture because of the great differences in thickness of the parts. In order to obtain radiographs of all the door it was necessary to make gamma radiographs. For this purpose the isotope Cs^{137} was used and about 100 radiographs (24 × 30 cm) were made.

A Modification of the Method for the Determination of the Current Efficiency in Aluminium Electrolytic Tanks. Z. ORMAN, A. PRADZYNSKI, Instytut Metali Niezelaznych; Instytut Podstawowych Problemów Techniki, Polska Akademia Nauk, Warsaw, Poland

The method for the determination of the current efficiency of aluminium furnaces described first by Rempel and Popow was improved by Bozoky and Vördös by using the radioisotope Au^{198}. In that work master alloys of aluminium with Au^{198} were made, and cylindrical samples of the master alloy of high specific activity were measured by means of a cylindrical G-M tube with a lead absorber inserted between the tube and the sample in order to minimize the intensity of radiation.

Such an arrangement cannot give exact results because of the bremsstrahlung produced from the radiation emitted by Au^{198} and scattering of the γ-radiation by the absorber.

In order to obtain better accuracy the specific activity of the master alloy was measured after dilution with a known quantity of pure aluminium. In that way samples of diluted master alloy and samples taken from the electrolytic tank were of the same order of specific activity and could be measured without any absorber.

Radioactivation analysis was employed in order to facilitate the application of this method in the aluminium plant and to avoid all restrictions and dangers connected with the handling of unsealed radioactive sources outside special radioisotope laboratories.

Inactive gold was introduced into the master alloy and into the smelting bath in the electrolytic tank. The concentration of gold in samples of both the master alloy and the smelt was then measured after irradiation of the samples in a nuclear reactor.

The Production of Radioisotopes with a Betatron Using an Internal Bombarding Technique. H. MORINAGA, Department of Physics, Tohoku University, Sendai, Japan

A new technique for producing radioisotopes of high specific activity with a betatron has been developed and is being used successfully. Materials to be activated are placed inside the doughnut at the end of a blind cylinder inserted from outside; thus samples are bombarded under one atmosphere just behind the bremsstrahlung target where the X-ray density is extremely high. The maximum electron energy is 25 MeV and at 50 cycles operation the flux density at the sample is about 10,000 r/min. The saturation activity of Cu^{62} produced on a small

piece of copper about 1 mm × 5 mm × 10 mm exceeded one millicurie and the highest specific activity obtainable was approximately 500 times that produced in a conventional arrangement.

So far, this internal target technique is being used only for nuclear spectroscopical work. The smallness of the target material is extremely suitable for beta and gamma measurements and also for the chemical treatment when necessary. Using the internal target, seven new species of radioactive isotopes (Co^{63}, Ga^{75}, As^{81}, In^{121}, In^{123}, Tm^{173} and Tm^{175}) have been identified and four new isomers have been found in addition to the successful production of many other isotopes for spectroscopical research.

The ease and effectiveness of such a bombarding technique should open a quite new use for the betatron, since a medical, industrial as well as research betatron may serve as a tool for isotope production by installation of an internal target of this type. Some isotopes are more conveniently made by photo-reactions using a betatron. Short lived isotopes which are often more convenient in various applications because of their fast decay and usually high energy radiation may be made readily without any additional skill other than operation of the betatron and handling of the radioisotopes. N^{13}, C^{11} and Cl^{34} are probably of greatest interest. The same technique is also applicable to small synchrotrons.

Wear Studies in the Shearing Process by Means of Irradiated Tools. T. Sata, K. Abe and K. Nakajima, Institute of Physical and Chemical Research, Tokyo, Japan

Tool wear in the shearing process of sheet metals was studied with punches and dies of high speed steel irradiated in an atomic pile. Circular disks of 10 mm in diameter were punched from sheet metal of 0·5 mm thickness of low carbon steel, stainless steel and silicic steel in dry and lubricated states. After punching, the radioactivity of the external surfaces of the disks and internal surfaces of the holes cut in half was measured with a Geiger-Müller counter. When the radioactive die was replaced by a non-active one, little radioactivity was detected on the exterior of the disks, while the radioactivity of the holes scarcely varied. This proved that the wear of the die can be found from the radioactivity of the disks and that of the punch from the radioactivity of the holes. By this method the wearing of punch and die was followed by using different lubricants and sheet metals with the following results.

(1) At the beginning of punching, the wear rates of both punch and die are very large but rapidly decrease, becoming eventually stationary after punching about four to five hundred pieces.
(2) The wear of the punch is more severe by about 20% than that of the die.
(3) Lubricants with extreme pressure additive, such as chlorine, phosphorus or sulphur, reduce tool wear, while refined mineral oils have little effect.
(4) The largest tool wear is detected in punching the harder sheet metals. Tool wear in punching stainless steel is about three times, and in silicic steel about six times as large as that of low carbon steel.

Application of Radiochemistry to the Preparation of High-Purity Silicon. T. Ichimiya, H. Baba and T. Nozaki, Electrical Communication Laboratory, Nippon Telegraph and Telephone Public Corporation, Tokyo, Japan

In order to obtain elementary silicon of transistor grade, several methods of purification have been tried, and among them, the iodide method is believed to be promising. Making use of radiochemical techniques, the present authors studied the behaviour of trace impurities during the purification by the iodide process, the determination of them, especially of halogens, in the resultant high-purity silicon, etc, in order to improve the method and establish an industrial procedure. The following four steps were used to purify crude silicon tetraiodide obtained by the iodination of raw silicon: (1) recrystallization from toluene, (2) sublimation, (3) fractional distillation, (4) zone refining.

To control the entrance rate of iodine vapour in the course of synthesis of the silicon tetraiodide, the utilization of the absorption of a soft γ-ray, which is strongly absorbed by iodine but only slightly by materials of low atomic number, was attempted. Behaviour of phosphorus as impurity at the recrystallization stage was studied by using p32 as tracer, and it was elucidated that the hydrolysis products formed on contact with moisture or by the addition of some water play, by virtue of their high adsorptivity, the predominant role in purification. The same phenomenon was observed in the zone refining step. Use was made of neutron activation analysis to determine the efficiency and to remove arsenic impurity at each of the purification steps and also to determine several kinds of trace impurities in the elementary silicon prepared by thermal decomposition of the purified iodide.

A suitable method of neutron activation analysis of trace iodine in high-purity silicon was developed and applied to samples prepared as above and those with further purification. The results indicated that iodine was the predominant impurity remaining persistently after a vacuum heating or zone refining process. Simultaneous determination of chlorine, bromine and iodine was also carried out to analyse

samples purified other than by the iodide method. The results indicated that most of the high-purity silicon contained a considerable quantity of a halogen.

Application of Radioisotopes to a Gas Chromatographic Detector for Direct Indication of Concentration. L. WIESNER, W. J. SCHMIDT-KÜSTER and GG. R. SCHULTZE, Institut für Erdölforschung, Hannover, Germany

During the last few years, numerous types of detecting devices, including ionization detectors, for gas chromatographic work have been developed. The quantitative evaluation of chromatograms suffers from the limited accuracy in measuring peak areas.

It appeared to be possible to overcome these difficulties with a detector based on the principle of ionization by nuclear radiation, but operated as a counter. The possibility of realizing this idea is given by the fact that the addition of organic vapours to rare gases lowers the voltage of the plateau characteristic of a counter. The detector consists of a flow type counter viewing a radioisotope source of ionizing radiation. A suitable scaler is used in connexion with this set-up. The power supply of the counter is chosen up to several hundred volts lower than the starting voltage of the unit operated on rare gas alone. When a fraction is emerging from the chromatographic column, the detector registers the incident radiation. The number of counts accumulated by the scaler over the "peak" is a direct measure of the concentration of the sample fraction under consideration. For preliminary experiments, a commercial methane-flow-counter was used and operated with argon. The performance of various counters of different geometry is described, and preliminary results about the sensitivity and the dependence of count rate upon concentration are discussed.

Experimental Comparison of Primary and Secondary Isotope Effects in Tritium or Carbon Labelled Compounds. H. SIMON and D. PALM, Technische Hochschule, Munich, Germany

The isotope effects (IE) in the phenylhydrazone formation of β-naphthaldehyde-(carbonyl-T), β-naphthaldehyde-(crabonyl-^{14}C), 3-phenylpropionaldehyde-1-T, β-D-mannose-1-^{14}C and β-D-mannose-1-T have been determined.

The IE in the formation of mannose-(1-^{14}C)-phenylhydrazone depends on whether the reaction is carried out immediately after the mannose has dissolved or after complete mutarotation. In this reaction the IE in β-naphthaldehyde-^{14}C gives an expected value of 1·06, whereas the tritium labelled compound has an inverse IE of about 0·78. With the 3-phenylpropionaldehyde (carbonyl-T) the IE is 1·1.

Though the IE of both tritium labelled compounds are different in direction, the frequency shift of the carbonyl group in the IR-spectrum of the corresponding deuterium labelled compounds shows the same direction and magnitude.

Therefore the direction of the secondary IE cannot be predicted from the frequency shift of the reacting groups which is caused by the influence of α-substituted hydrogen isotopes.

^{187}Os-Isotope Abundance Anomalies in Terrestrial and Meteoritic Osmium and an Attempt to Determine Re/Os-Ages of Iron-meteorites. W. HERR, W. HOFFMEISTER and J. LANGHOFF, Max-Planck-Institut für Chemie (Otto-Hahn-Institut), Mainz, Germany, and J. GEISS, B. HIRT and F. G. HOUTERMANS, Institute of Physics, University of Bern, Bern, Switzerland

The isotopic composition of a large number of Os-samples from terrestrial platinum ores and from iron meteorites has been investigated by mass-spectrometry. The observed isotope-ratios ^{187}Os:^{186}Os in Os/Ir-ores and in Os-samples, extracted quantitatively from iron meteorites, vary in the limits from 0·88 to 1·41. These variations may be explained by the production of radiogenic Os following the decay of ^{187}Re, a natural β-emitter with the lowest known β-energy. Neutron activation analysis proves that Re and Os are common trace elements in iron meteorites.

As dating of these bodies by conventional methods suffers from enormous difficulties, the application of the Re/Os method has been studied.

From our experiments a primordial ^{187}Os:^{186}Os ratio is derived and "minimum ages" are discussed. They differ widely and are found presumably in the range from 3·7 to 5·6 . 10^9 years. In addition the half-life of ^{187}Re has been checked again by comparing the K/Ar age of a felspar with the Os/Re age of a cogenetic Re-containing molybdenite.

The radiochemical procedure is described in some detail.

Studies on the Mechanism of Sugar Osazone Formation Using Tritium Labelled Compounds. F. WEYGAND, H. SIMON, J. -F. KLEBE and K. D. KEIL, Technische Universität, Berlin–Charlottenburg, Technische Hochschule, Munich, Germany

In the reaction of glucose-1-T or mannose-1-T with phenylhydrazine to phenylosazone, the osazone formed shows, depending on the reaction conditions, the same or less radioactivity than the labelled hexoses. The different loss of tritium in the osazone formation depends on the rate determining step or on

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the added catalyst which may change the isotope effect of splitting the carbon-tritium bond. It is excluded that the loss of tritium is caused by an unspecific exchange or a secondary kinetic isotope effect.

The dependence of the magnitude of the isotope effect on reaction conditions was studied with 1-desoxy-*p*-toluidino-D-fructose as a model.

A strong incorporation of tritium at C^1 occurs in the formation of osazone from unlabelled sugar in tritium-containing water. It follows from these results that the osazone is formed partly via 1-desoxy-1-phenylhydrazido-D-fructose, which means that the Amadori rearrangement as postulated by Weygand as route *B* takes place. Therefore it can be concluded that the mechanism postulated by Fischer is not valid and that another part of the osazone formation follows a route (route *A*) which involves a partial Amadori rearrangement and is therefore closely related to mechanism *B*.

Preparation of very Small Amounts of Tritium Labelled Polyphenols and the Isolation of the Tritiated Compounds by "Normal Freezing". H. SCHILDKNECHT and F. SCHLEGELMILCH, Institut für Organische Chemie, Universität Erlangen, Erlangen, Germany

The sensitivity of paper chromatography can be improved by the application of tritium as an indicator.

0·01 mg to 0·1 mg resorcinol were labelled by an exchange reaction with tritiated water (5 curies/ml) in alkaline medium and in the presence of a platinum-oxide catalyst. In addition to the desired exchange there was noted a destruction of the organic substance. The best results however were obtained without a platinum-oxide catalyst and a longer reaction time (10 hr) and still better at an increased temperature, up to 100°C. The specific activities in these cases were 1:4 . 5:30. When labelling hydrochinone and pyrogallol only mild conditions were employed.

The separation of these small quantities of radioactive compounds from the tritiated water was made without loss by "Normal Freezing". A reaction tube (0·6 cm in diameter) with the solution which was to be concentrated, was lowered slowly into a copper-tube cooled by a freezing mixture. During this procedure the liquid above the ice is stirred vigorously. Thereby the intensity of agitation has an influence on the enrichment effect. The crystallization rate was 6 cm/hr and the cooling mixture had a temperature between −40 and −50°C. For insulating the labelled compounds a very small part of the frozen solution on the top of the ingot was melted and repipetted onto a paper chromatogram. This was developed with a mixture of benzene/butanol/water 9:1:10. After drying of the paper chromatogram the radioactive compounds were located quantitively either by a technique of "scintillation autography" by Wilson or by scanning with a flow counter. After these manipulations the specific activity e.g. of resorcinol was—regarding all sources of error—128,500 DPM/mg or 2·23 c/mg.

Principles and Applications of Heterogeneous Isotope and Ion Exchange on the Surface of Ionic Crystals. K. LIESER, Eduard-Zintl-Institut, Technische Hochschule, Darmstadt, Germany

Ionic crystals which are in contact with an electrolytic solution exchange isotopic and non-isotopic ions on their surfaces. These events are treated quantitatively and measured in relation to the time factor.

In general, two kinds of event are to be observed: exchange with the surface ions, and recrystallization of the ionic crystals in the solution. During ion exchange recrystallization is only observed if mixed crystals are formed.

The velocity of the ion exchange on the surface is normally determined by the surface reaction, not by diffusion in the solution.

The following systems will be discussed as examples of isotope and ion exchange reactions:

$^{90}Sr^{++}/SrSO_4$, $^{90}Sr^{++}/CaSO_4 \cdot 2H_2O$, $^{90}Sr^{++}/BaSO_4$.

These analyses are important for the separation of carrier-free nuclides from aqueous solutions.

One practical application is the separation of Sr-90 on barium sulphate columns.

Radioisotopic Control of Wear on the Suspension Bearing of Large Turbogenerators. KOL, KOPETZKÝ, FRINTA, Státní vyzkumný ústav materiálů a technologie, Prague, Czechoslovakia

The suspension bearing has a diameter of 3500 mm and the quantity of coolant oil used is 90 hectolitres. Owing to the large dimensions of the bearing, it was impossible to use standard methods for measuring wear. A new method was evolved whereby a few small areas on the contact surface of the bearing were activated and the loss in activity measured by a Geiger-Müller counter, mounted 20 mm below the activated bearing. This method was used to study the kinetics of wear on the bearing (material K 80) used in turbogenerator set TG-1 at Slapy hydro power station from the time the turbine was first started up over a period of 3600 hours. It was found that the main wear occurs during the first 400 hours, and that it is during this period that there is the greatest danger of seizure. Radioactive silver was

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used to activate the bearing. The accuracy of measurement achieved was high, since it was possible to detect wear of the order of 1 to 2 microns.

Some Possible Uses of Radioisotopes in the Rubber Industry. J. Šimorda, M. Možíšek, L. Klimánek, J. Staroba, Výzkumný ústav gumárenské a plastikářské technologie (VUGPT) Gottwaldov, Czechoslovakia

Out of the many possible uses of radioisotopes in rubber technology special interest attaches to measuring the wearing qualities of tyres, checking the even quality of tyre rubber, and non-contact measuring of rubberized fabrics.

The wearing quality of tyres can be gauged more rapidly and more accurately in road tests by using the absorption method for measuring the reduction in thickness of the tread or by measuring the activity of the rubber worn down on the road.

In the former case we use point sources placed at an optimum depth beneath the surface of the tread. Using experimentally determined absorption characteristics it is possible to establish the change in thickness of the layer of tread above the source as a function of the change in the impulse counting-rate (per minute) measured above the surface of the tread.

Reference is made to the types of point sources used, namely those containing thallium-204, and the possible uses of this method are indicated.

In the latter case it is possible to observe the effect of the running conditions (speed of the vehicle, load, road surface and so on) on the wearing properties of motor vehicle tyres.

The paper describes the diffusion activation of the surface of the tread of a vulcanised tyre and indicates how the measuring and recording apparatus is used.

In order to test the even quality of tyre rubber, which can only be checked with difficulty by means of the standard marketed equipment, use is made of suitably labelled tested additives or else of radioscopy.

The method actually described is the radioscopy method, which makes it unnecessary to add active materials to the test blends.

Reference is made to the possibility of testing vulcanised and non-vulcanised specimens, and specimens selected from a stock of finished articles.

The authors describe the sources used, the geometry of measurement and the method used for evaluating the measurement data.

The advantages of non-contact thickness gauging of coatings and coverings during processing of the rubber are sufficiently well known.

Some difficulty arises in ensuring the long-term stability of the testing and measuring equipment and in connexion with the fact that this equipment is dependent on the chemical composition of the covering measured.

The authors refer to certain advantages of using a calibrating diaphragm in conjunction with simple apparatus in the event of changes in production, and indicate what is entailed in switching over from measurement to automatic regulation.

Stereochemistry and Radiochemistry of Deamination Reactions. C. J. Collins and B. M. Benjamin, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

The utility of the combined radiochemical-stereochemical technique in detecting which side of the migration terminus is attacked by each of two migrating groups during reactions involving 1,2-shifts, has previously been demonstrated. These same techniques have now been applied to the mechanisms of the deaminations of (1) optically active *threo-* and *erythro*-1,2-diphenyl-1-amino-2-propanol, (2) optically active *threo-* and *erythro*-1-phenyl-2-*p*-tolyl-1-amino-2-propanol, and (3) to optically active 1,1-diphenyl-2-aminopropane. Both stereospecific and nonstereospecific carbon-14 labels were employed. In each case the optical isomers produced were isolated, and the fate of each label was determined. Appropriate control experiments were performed with reactants which were labelled both with carbon-14 and with deuterium. The absolute configurations of reactants and products for each reaction were studied through synthetic sequences which do not affect the optical integrity of the asymmetric centres. From these data it has been possible to arrive at certain definite conclusions concerning the mechanisms of the foregoing reactions. For example: (1) the fractions of each reaction proceeding through *cis-* and *trans-*transition states have been evaluated, and (2) new information has been gained concerning the importance or unimportance of "neighbouring group participation".

Finally, although classical techniques have been employed to clarify the stereochemistry of the families of compounds studied, a novel radiochemical method has also been used for the same purpose.

Carbon-14 Isotope Effects in the Decarboxylation of 2-Benzoylpropionic acid. E. M. Hodnett and R. L. Rowton, Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma, U.S.A.

2-Benzoylpropionic acid decomposes at temperatures near 70°, giving carbon dioxide and propiophenone. The kinetics of this decarboxylation have been studied under a variety of conditions; the initial portion of each reaction showed first-order

kinetics from which reaction rate constants could be obtained. The results are in accord with the cyclic, concerted mechanism proposed for the decarboxylation of β-keto acids.

Three syntheses of 2-benzoylpropionic acid were made with carbon-14 in the 1-, 2-, and carbonyl positions respectively. The isotope effect in the decarboxylation of each acid at 78° was determined by stopping the reaction at various percentages of completion and radioassaying the products or the remaining reactant.

Evaluation of Deuterium Isotope Effects in Photochemical Reactions of Formic-d Acid by Use of Carbon-14. G. A. Ropp, Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

The usefulness of measured values of primary and secondary deuterium kinetic isotope effect ratios in the study of organic reactions is well known. However, measurement of such ratios by direct methods is sometimes difficult. An indirect method which can be used to circumvent difficulties in some cases is illustrated by the determination of the primary deuterium isotope effects in the following vaporphase reactions:

$$CHOOH + Cl_2 \xrightarrow[\text{light}]{\text{visible}} 2HCl + CO_2 \qquad (1)$$

and

$$HCOOH + Br_2 \xrightarrow[\text{light}]{\text{visible}} 2HBr + CO_2 \qquad (2)$$

For the evaluation of k_D/k_H, the ratio of specific rate constants for reaction of formic-d acid and formic acid, a 50:50 mixture of DCOOH and $HC^{14}OOH$ was added to enough chlorine (or bromine) to effect reaction of approximately 5% of the mixture of acids. The carbon-14 dioxide produced was precipitated as barium carbonate-C^{14}, the specific activity (S_5) of which was then determined by radioassay of the gas released when a sample was acidified. The specific activity (S_{100}) of the barium carbonate-C^{14} representing 100% reaction of a portion of the 50:50 mixture of DCOOH and $HC^{14}OOH$ with excess chlorine was also determined. The equation,

$$\frac{k_D}{k_H} = (R + 1)\left(\frac{S_{100}}{S_5}\right) - R \qquad (3)$$

where R is the molar ratio of $HC^{14}OOH$ to DCOOH in the mixture of acids used, was derived making the reasonable assumption that the carbon-14 isotope effects in reactions (1) and (2) are negligibly small in comparison with the deuterium isotope effects. Using equation (3), k_H/k_D values, 2·0 and 2·7, were calculated for reactions (1) and (2) respectively.

An earlier study (Ropp, Danby, and Dominey, 1957) showed that reaction (1) was accompanied by a much smaller carbon-13 kinetic isotope effect than reaction (2). This was taken as an indication that the carbon-hydrogen bond is stretched more in the transition state for reaction (2) than for reaction (1). The presently reported difference between the corresponding deuterium isotope effects is less pronounced though in the same direction as the difference between the carbon-13 effects. A reasonable conclusion is that bromine-hydrogen bonds formed in the transition state for reaction (2) largely compensate the stretching of the carbon-hydrogen bond.

The Self-induced Exchange Between Tritium Gas and Hydrocarbons. T. H. Pratt and R. Wolfgang, Department of Chemistry, Yale University, New Haven, Connecticut, U.S.A.

The exchange of tritium atoms between T_2 gas and methane, as induced by the radioactive decay of the tritium has been investigated. This type of exchange forms the basis of the labelling process developed by Wilzbach.

Two distinct mechanisms appear to be involved and are quantitatively evaluated. (1) Decay of one of the atoms in T_2 yields HeT^+. This species reacts rapidly with CH_4 to give the excited ion CH_4T^+ which promptly decomposes to CH_2T^+. CH_3T is then formed by hydride ion exchange with CH_4. This postulated mechanism shows the required first order dependence on the T_2 pressure and is unaffected by additives such as Xe, which due to their low ionization potential, act as ion scavengers. (2) Beta radiation from the tritium decay produces CH_4^+ which forms CH_5^+ on collision with another methane molecule. The CH_5^+ is then postulated to undergo an exchange with T_2 to form CH_4T^+ and finally CH_3T. This mechanism gives rise to an observed term in the kinetics involving a 3/2 power dependence on tritium pressure and is sensitive to ion scavengers.

Other mechanisms are considered but excluded as incompatible with observed kinetics, the action of added small amounts of Xe and NO, and known energetics. The origin of tritiated products other than methane is discussed in terms of related mechanisms. It appears that the postulated processes can be extended to Wilzbach labelling reactions in general.

Adsorption of the Elements from Nitric Acid by Anion Exchange*. R. F. Buchanan and J. P. Faris, Argonne National Laboratory, Lemont, Illinois, U.S.A.

The adsorption characteristics of some 60 elements in nitric acid media were studied with a strong base

* Based on work performed under the auspices of the U.S. Atomic Energy Commission.

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anion exchange resin. Radioactive tracers were used to determine the distribution coefficients after a preliminary survey by optical emission spectrographic techniques. The coefficients for those elements which were not strongly adsorbed were determined from elution data while for those which were strongly adsorbed batch equilibrium data was used. When it was not possible or practical to use tracers, the adsorption data was determined spectrograhpically.

Most elements were not adsorbed in the range of acid concentrations studied (1M–14M). $U^{(VI)}$, $Th^{(IV)}$, $Bi^{(III)}$, $Zr^{(IV)}$, $Pu^{(IV)}$, $Np^{(IV)}$ and some of the light rare earths exhibited an adsorption maximum at approximately 8M nitric acid. $Re^{(VII)}$ $Pd^{(II)}$, $Au^{(III)}$ and $Ru^{(IV)}$ were decreasingly adsorbed with increasing acid concentration.

The nitric acid medium is rather selective for the adsorption of thorium, neptunium and plutonium and can be used for their separation as an interference and/or for their quantitative determination. This system is readily adaptable to sequential analysis in conjunction with other anionic systems already reported in the literature, i.e., hydrochloric acid, hydrofluoric acid and hydrochloric-hydrofluoric acid mixtures. The information presented here has applications in research and analytical problems where fission products are involved and in process chemistry where large scale separations are required. Anion exchange provides a fast separation using simple techniques and inexpensive expendable equipment.

Some data showing the effect on the adsorption characteristics when the free acid content was kept low and the nitrate concentration varied by the addition of ammonium nitrate are also given.

Mutual Separation of Californium and Curium by Extraction with Acidic Phosphonates. D. F. Peppard, G. W. Mason and I. Hucher, Argonne National Laboratory, Lemont, Illinois, U.S.A.

Although, in general, the mutual separation of a pair of actinides (III) is readily accomplished by ion exchange, there are certain difficult separations to which the technique of liquid–liquid extraction may be applied with profit. An example is the californium-curium separation.

In its essentials, this problem is two-fold: to isolate the Cf in high yield and high purity and to isolate the Cm in a form consistent with ready conversion to target material for re-bombardment. Liquid–liquid extraction, employing acidic phosphonates, is reported for the first time as extractants, offers a promising solution to this problem.

The acidic phosphonates, $\{(G'O)(G)PO(OH)\}_2$, where G′ and G are generalized organic groups, are dimeric and are represented as $(HY)_2$ in the composite extraction equilibria:

$$M_A^{+3} + 3(HY)_O^2 \rightleftharpoons M(HY_2)_O^3 + 3H_A^+ \quad (1)$$

$$K = k_1[(HY)_2]_O^3/(H^+)_A^3 \quad (2)$$

where the subscripts A and O refer, respectively, to mutually equilibrated aqueous and organic phases, the carrier diluent being toluene.

Direct third-power extractant and inverse third-power acid dependencies, indicated by Expression (2), have been confirmed for both Cf and Cm in systems employing $HClO_4$, HCl and HNO_3 at constant μ and utilizing phosphonates with G′ fixed as 2-ethyl hexyl and with G = 2-ethyl hexyl, phenyl and chloromethyl.

As G varies in the above order, k_1 (from Expression (1)) for Cm in a 1·0 μ perchlorate system becomes $2{\cdot}6 \times 10^{-4}$, 2·6 and $5{\cdot}3 \times 10^{2}$. The range in k_1 is a factor of 2×10^6.

The k_1 for Cf, although varying comparably, does not vary identically as the k_1 for Cm. Consequently, the β for the Cf–Cm separation is different for the different extractants.

The β value of 110, realized in the (2-EtHex O)(Φ)PO(OH) versus aqueous HCl (μ = 1·0) system, makes the mutual separation of Cf and Cm by liquid–liquid extraction a simple problem.

It is suggested that important new separations systems may be discovered through the investigation of the effect of varying both G′ and G.

Vapour–Liquid Equilibria of Tritium-Hydride in Hydrogen and Tritium-Deuteride in Deuterium. J. Bigeleisen, Chemistry Department, Brookhaven National Laboratory, Upton, L.I., New York, U.S.A., and E. C. Kerr, Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico, U.S.A.

Vapour–liquid equilibria have been studied for the systems HT in e-H_2 and DT in e-D_2 over the temperature range 14–30°K and 18·7–32·5°K respectively. The solutions studied were dilute ($\sim 10^{-8}$ M) and measurements were made by counting aliquot samples of the liquid and gas phases, which had been brought to thermal and isotopic equilibrium. Considerable care was given to achieve isotopic equilibrium, which was effected by circulation of the gas through the liquid with a piston pump. Reflux of the vapour above the liquid was avoided by a positive thermal gradient.

The solutions obey Henry's law over the range of concentrations studied. The enrichment factors, 3·7 and 1·4 for HT in H_2 and DT in D_2 respectively, near the triple points of the solvents show that low

temperature distillation is an effective process for the separation of tritium from protium and deuterium. The separation factors go to unity at the critical temperature. The separation factors for HT from H_2 are lower than those observed for the isobaric pair D_2–H_2. This behaviour is in accord with predictions of the structural effect on the vapour pressures of isotopic molecules. HT behaves as a "light" molecule compared with D_2. The results are discussed in terms of quantum effects. A model treatment of the system in terms of first order quantum effects, although not applicable to the system, gives results in good agreement with experiment. The experimental data support refinements in the quantum theorem of corresponding states to include a coupling between translation and rotation.

Radiotracer Techniques in the Study of Corrosion by Molten Fluorides. W. R. GRIMES, G. M. WATSON, J. H. DEVAN and R. B. EVANS, III Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

When Inconel (Nominal composition: 15% Cr, 5% Fe, balance Ni) or Inor-8 (Nominal composition: 7% Cr, 16% Mo, balance Ni) is exposed to a molten fluoride mixture containing reducible material chromium is selectively oxidized and removed from the alloy. When UF_4 serves as the oxidant in a polythermal test system the temperature-sensitive equilibrium

$$2UF_4 + Cr^0 = CrF_2 + 2UF_3$$

provides a mechanism by which the alloy at high temperature is depleted and the alloy at low temperature is enriched in chromium. On the other hand, the reaction

$$FeF_2 + Cr^0 \rightarrow CrF_2 + FeF_2$$

is essentially complete at all practicable temperatures; use of FeF_2 as the oxidant, accordingly, removes chromium from all portions of the system. In either case, the rate of corrosion is controlled by rates of diffusion of chromium within the alloy.

By use of radiotracer Cr-51 the self-diffusion coefficients for chromium in Inconel and Inor-8 and the applicability of these values to alloys under corrosive conditions have been evaluated.

Overall coefficients have been obtained by measuring (1) depletion of Cr-51 (charged as CrF_2) to non-corrosive fluoride melts in alloy capsules and (2) by comparison of measured total radioactivity of exposed alloy specimens with that of the salt to which they were exposed. In addition, coefficients were obtained from measurement of tracer concentration profiles through successive electropolishings of the specimens. The overall coefficients and those obtained from electropolishing experiments agree very well for Inconel at high temperatures and for Inor-8 at all temperatures. For temperatures below 750°C, coefficients obtained by electropolishing Inconel specimens are higher than the overall values; the bulk diffusion process is not uniform for this case. In all cases, good agreement was found between the overall diffusion coefficients and those extrapolated from published data at higher temperature with generally similar Cr–Ni alloys.

Duplicate, polythermal loops of Inor-8 were used to circulate a non-corrosive fluoride melt containing Cr-51 (as CrF_2). One of these loops was sacrificed to evaluate takeup of Cr-51 by the alloy; the second was used to circulate a melt containing FeF_2 to obtain measurable removal of Cr from the alloy. Good agreement between observed behaviour and that predicted from the measured diffusion coefficients was obtained; this agreement suggests that the self diffusion coefficient for Cr is insensitive to changes in chromium content of the Inor-8 alloy.

Some Applications of Radioisotopes in Physical Chemistry—Two-Phase Equilibria and Packed Column Techniques. K. A. KRAUS, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

One of the most effective applications of radioisotopes in physical chemistry is the study of two-phase equilibria; our own studies for a number of years have been concentrated on ion exchange reactions with commercial organic and with new types of non-siliceous inorganic exchangers. With the former, the studies were carried out in depth covering at times most elements in the periodic table, the objective being comparison of functional relationships of many systems rather than the detailed study of a few. With the inorganic exchangers, the objective was also broad coverage of many systems, particularly comparison of large numbers of adsorbents. Since these studies required hundreds of thousands of analyses, they would have been almost impossible with conventional analytical techniques and the feasibility of such studies can be considered a direct outgrowth of the ready availability of radioactive tracers, and the steady increase in precision and convenience of counting techniques.

More recently, packed column techniques have been developed which with radioactive tracers and relatively simple equipment permit ready extension of studies of two-phase equilibria and studies of the kinetics of interfaces to higher temperatures (presently up to 200°C). Sampling and continuous monitoring techniques were used. Through adsorption and solubility studies, information on enthalpy and entropy changes of adsorption and ion exchange reactions is

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reported as well as information on beats of solution, activity coefficients in concentrated electrolyte mixtures, and on complexing reactions in high temperature aqueous systems.

Radioisotopes as Tracers for Reactions in Molten Fluoride Media. W. R. GRIMES, J. H. SHAFFER, R. A. STREHLOW, W. T. WARD and G. M. WATSON, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

Chemical reactions which may be useful for removing certain constituents from molten fluoride solution have been examined by use of appropriate radioisotopes and standard counting procedures. Classes of reactions studied have included:- (1) isotopic exchange between solute tracer and insoluble compound, (2) partition of solute between the melt and a solid solution of a similar compound, and (3) precipitation of the radioisotope as insoluble compound.

The radiotracer was generally added, along with inactive isotopes of the element under study, as fluoride to the previously purified solvent; occasionally the tracer was added as chloride or oxide and subsequently converted to fluoride by sparging the molten solution with anhydrous HF vapour. Samples of the melt were drawn for analysis, by counting or otherwise, by use of a filter-stick whose filtering medium was of sintered copper.

In typical experiments, radiotracer LaF_3 in LiF–NaF melts was shown tc exchange rapidly with inactive La_2O_3. A similar rapid exchange in this solvent occurred between radiotracer CeF_3 and inactive CeO_2; the electron transfer required in the latter case is apparently no barrier to the reaction. Addition of inactive CeF_3 to each system increased the radiotracer content of the solution in accordance with the mass-action principle.

When certain LiF–BeF_2 melts containing CeF_3 and rare earth fluorides are cooled the primary phase is a solid solution of the trifluorides. Equilibria such as

$$CeF_{3(d)} + LaF_{3(ss)} = LaF_{3(d)} + CeF_{3(ss)}$$

where d and ss indicate that the species is in molten solution and solid solution, have been evaluated for various fluoride pairs. No significant deviations from the simple mass action principle have been observed.

Separations of various species by selective precipitation of oxides from molten fluoride solutions have been demonstrated. From LiF–NaF melts, for example, Zr^{+4}, U^{+4}, Ce^{+3}, Sm^{+3}, and other rare earth trifluorides can be precipitated as oxides by addition of Li_2O, LiOH, CaO, BaO, or superheated steam. From LiF–BeF_2–ThF_4 mixtures, separation of UO_2 from thorium and from fission products such as rare earths can be made by selective precipitation of UO_2 with steam or with beryllium oxide.

The Variation of Solubility of Strontium Sulphate with Particle Size. E. V. ENUSTUN and J. TURKEVICH, Princeton University, Princeton, New Jersey, U.S.A.

Radioactive sulphur was used to study the variation of solubility of strontium sulphate with particle size. Synthetic methods were used to control the particle size ($d = 160 - 1000$ Å) and the size distribution was determined by electron microscopy. The separation of phases was carried out by centrifugation and the supernatant liquid was examined with the electron microscope to check for existence of peptized particles. The concentration of the dissolved $SrSO_4$ was determined by evaporation of an aliquot of the supernatant and determining the sulphur activity.

The results were found to follow the Ostwald Freundlich equation for solubility with the smallest particles in a given distribution determining the solubility. From the solubility data an interfacial tension of 84 ± 8 erg cm was obtained, a value much lower than previously reported in the literature.

The Ostwald Freundlich equation was extended to crystals of any geometry. Using this extended equation the interfacial tension of the different faces of strontium sulphate was calculated.

The data on variation of solubility with particle size and on the synthesis of particles of $SrSO_4$ were used to determine the size of the nucleus of $SrSO_4$.

Semiquantitative observations showed that the rate of solubility is much faster than the rate of growth.

Some Solvent Extraction Studies of Trivalent Metal Halides. R. J. DIETZ, J. MENDEZ and J. W. IRVINE, JR., Department of Chemistry and Laboratory for Nuclear Science, Massachusetts Institute of Technology, Cambridge, Massachusetts, U.S.A.

Radiotracer techniques have made possible physical-chemical studies of the distribution of $Ga^{(III)}$ and $In^{(III)}$ between aqueous HCl and HBr solutions and the organic solvents, bis(2-chloroethyl)ether and nitrobenzene. From measurements of the extraction coefficients over a metal concentration range of greater than 10^{10} and under conditions where the coefficient varies by a factor of 10^5 the empirical behaviour of these systems has been thoroughly explored. The data have been explained in terms of ionization of the complex acid, HMX_4, in these relatively high dielectric solvents.

From the variation of the extraction coefficient with metal concentration the ionization constant has

been calculated of the supporting electrolyte, HCl or HBr, in the non-aqueous phase using a method developed by Poskanzer.

Variation of the extraction coefficient with HX concentration can be used to calculate stability constants, k_3 and k_4, for the complex species MX_3 and MX_4 if values for k_1 and k_2 are available. Since these are aqueous phase reactions they are independent of the organic solvent used and excellent agreement is obtained for $In^{(III)}$–HCl, $k_3 = 0{\cdot}30$ and $k_4 = 0{\cdot}55$, using both bis(2-chloroethyl)ether and nitrobenzene. $In^{(III)}$–HBr gives $k_3 = 0{\cdot}06$ and $k_4 = 0{\cdot}012$ with bis(2-chloroethyl)ether as the extractant.

Attempts to evaluate the formation constants for gallium chloride and bromide complexes failed since the complex formation occurs over a very narrow range of acid concentration. Calculation from extraction data of the fraction, $(GaCl_4)/\Sigma Ga^{(III)}$, as a function of HCl concentration gave a quantitative agreement with the data obtained from ion exchange measurement by Kraus and Nelson.

Labeling of Organic Compounds by Electric Discharge in Tritium Gas. K. E. WILZBACH and L. M. DORFMAN, Argonne National Laboratory, Lemont, Illinois, U.S.A.

The gas exposure technique for tritium labeling has been used successfully for many organic compounds and has received wide acceptance. Use of this technique is somewhat restricted, however, since curie amounts of tritium and exposure times of several days are needed to supply sufficient energy to introduce even a small fraction of the gas into the compound.

It has now been found that use of an electrical discharge to promote ionization and excitation of the gas permits use of smaller quantities of tritium and shorter exposure times.

In the new technique, a small amount, about 0·5 g, of the compound to be labeled is placed in the lower cup-shaped electrode of a glass vessel and tritium gas is admitted to a pressure of 5–15 mm. The lower electrode is grounded and the upper electrode is connected to a Tesla coil leak-tester. A discharge at approximately 100 μA and 1000 volts is passed through the gas for a few minutes. As in the gas exposure technique some decomposition occurs, and the compound must be purified from tritiated by-products. Activities in the range of 3–20 millicuries per gram, comparable to those produced by simple exposure to tritium gas, have been obtained with several organic compounds.

A particularly attractive feature of this technique is the possibility of use in laboratories not equipped to handle the larger amounts of tritium required by the gas exposure method.

Radioisotopes in the Physical Chemistry of the Corrosion Process and its Inhibition. G. H. CARTLEDGE, Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

The fundamental study of electrochemical processes related to corrosion and its inhibition is an increasingly important branch of physical chemistry. Certain of the factors entering into such processes are: (a) adsorption phenomena of different types, (b) ion-exchange properties of passive films (with corresponding influences on phenomena related to zeta potentials), and (c) the electrochemical kinetics of both anodic and cathodic processes across the interface between a metal and its corrosive environment. The availability of radioisotopes has made possible certain studies of these phenomena that could not be made previously with conventional materials.

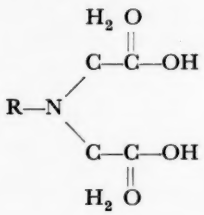
The element technetium, a homologue of manganese in the periodic system, has been found uniquely suited to certain of these studies. The nuclear properties of the element are extremely fortunate in that the half life is somewhat over 200,000 years, and the radiation is a weak beta activity which is ample for autoradiographic and counting techniques, but presents no radiation hazard in the quantities required. The chemical properties of technetium compounds are summarized and contrasted with those of corresponding Cr^{51} compounds and those of molybdenum and tungsten so much used in studies of inhibition.

Selected experimental studies are given as examples of the uses to which technetium has already been put in this type of work. Among these are empirical studies of its action as a very efficient inhibitor of the corrosion of iron, with inclusion of long-term observations of surface activity. Other studies with both Tc^{99} and I^{131} have demonstrated the significance of competitive adsorption of ions in the determination of the kinetics of the corrosion and inhibitory processes. As a third example, a description is given of how the unique properties of technetium have permitted a clear discrimination between the relative contributions of oxygen and the oxidizing inhibitor in the maintenance of passivity.

Elucidation of a Secondary Chemical Interaction in an Ion-exchange Resin by a Radioisotope Dilution Method. J. A. MARINSKY and J. KRASNER, University of Buffalo, Buffalo, New York, U.S.A.

Radioisotopes are being employed at the University of Buffalo to enhance studies of the solution chemistry of different ion-exchange materials. Particularly of interest is the application of an isotope dilution

method to the investigation of the dissociation constants of the acid form of the Dowex-Chelating Resin A-1. This resin is comprised of a styrene-divinyl benzene copolymer matrix within which are attached iminodiacetate active groups as shown below, R indicating the copolymer matrix:



It is possible to estimate dissociation constants of the acid form of the resin from controlled neutralization of the resin with NaOH assuming (1) that the functional groups are so weakly acidic that essentially there are no H_3O^+ ions in the gel phase, (2) that the salt form is completely ionized, and (3) that the distribution of H_3O^+ and Na^+ ions between resin and solution are the same as in the exchange of these ions with Dowex-50 of cross-linking similar to that of Dowex A-1. If isopiestic measurements are also made corrections for activities of the components in the resin phase can be included in the evaluation of these constants.

During an experiment weighed portions of the acid form of the resin, converted from the sodium form with HCl and stored in an HCl atmosphere due to 6M HCl, were equilibrated for this purpose with predetermined quantities of NaOH in a 0·1 M NaCl solution containing a measured amount of the ~2·6 yNa^{22} nuclide. The concentration of Na^+ and H^+ ions in both phases at equilibrium were then evaluated from the solution pH and the observed distribution of Na^{22} between the resin and solution phases.

Double scrutiny of the neutralization reaction that is obtained from this technique has shown the apparent absence of stoichiometric exchange of sodium ions in the solution for hydrogen ions in the resin. This behavior has been partially attributed to sorption of HCl chemically to the nitrogen of the functional group since only a fraction of the sorbed HCl is removed during equilibration with 0·1 M NaCl. The remainder appears in the aqueous phase as NaCl only after neutralization with NaOH. Affirmation of this is from chloride analysis of the aqueous phase after equilibration. Sodium does not enter the resin phase significantly until the bound HCl is almost completely neutralized. An unexpected acidic property of the resin, attributable to the nitrogen of the functional group appears to be demonstrated from these data.

Application of Radioisotopes to the Investigation of the Kinetics and Mechanism of Reactions of Some Inorganic Complex Compounds. G. M. Harris, Department of Chemistry, University of Buffalo, Buffalo, New York, U.S.A.

Radioisotopes are invaluable tools in the study of many types of inorganic chemical reactions, particularly those involving complex ionic substances in aqueous solution. One important approach is through research on the rates and mechanisms of isotopic exchange processes. For example, a series of studies has been made of the exchange between carbon^{14}-labelled "free" carbonate and the ligand carbonate in octahedral complex ions of the type $CoA_2CO_3^+$, where A = $2NH_3$, ethylenediamine (en), propylenediamine (pn), or trimethylenediamine (tn). These studies have led to a rather thorough understanding of the nature of this kind of ligand substitution reaction, and of the part played by the non-exchanging amine ligands in the process. Similar studies of oxalate exchange with tris-oxalate complexes of the form $M(C_2O_4)_3^{-3}$, where M = $Co^{(III)}$, $Cr^{(III)}$, or $Rh^{(III)}$, have been equally fruitful.

An alternative technique, applicable only when using low atomic weight radioisotopes such as carbon^{14}, is to observe the equilibrium or kinetic isotope effects in the reaction of interest. It has, for instance, been possible to interpret differences in the ligand carbonate exchange mechanism of $Cotn_3CO_3^+$ and $Cotn_2CO_3^+$ on the basis of equilibrium isotope effect measurements made on the carbonate exchange reaction. Similarly, data on the kinetic isotope effect in the acid-catalysed equation of the $Co(NH_3)CO_3^+$ ion has supported deductions as to the nature of the rate-determining bond-breakage step in such reactions.

Finally, the mechanistic path of certain atoms or radicals in inorganic reactions, where a choice between alternative explanations must be made, is frequently facilitated by a radioactive tracer experiment. An example is the proof that cyanide does not appear as a rapidly exchanging intermediate in the oxidation of thiocyanate ion by hydrogen peroxide, although cyanide is an important end-product.

The Rates and Orders of Electron Exchange Reactions in Mixed Solvents Using Tracer Techniques. E. S. Amis, University of Arkansas, Fayetteville, Arkansas, U.S.A.

Very interesting results on the rate and mechanism of the electron exchange reaction between $U^{(IV)}$ and $U^{(VI)}$ in hydrochloric acid solutions involving pure and mixed solvents have been obtained using uranium^{233} as a tracer.

In the solvent range from pure water through various percentages of ethanol to pure ethanol the

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orders with respect to the reaction components were determined. The zero and near zero orders were proved not to be due to wall or light effects. Assuming the hydrolysis equilibria:

$$K_1 = \frac{[UOH^+][H^+]}{[U^{+4}]} \quad (1)$$

and

$$K_2 = \frac{[UO_2OH^+][H^+]}{[UO_2^{++}]} \quad (2)$$

and assuming the rate expressions:

$$\frac{dx}{dt} = k' [UOH^{+3}]^2[UO_2OH^+] \quad (3)$$

and

$$\frac{dx}{dt} = k'' [UOH^{+3}][UO_2OH^+] \quad (4)$$

equations for rates were derived which, under certain limiting conditions, accounted for the observed orders over the greater part of the range of solvent composition.

Ions similar to the complex species postulated to explain the kinetics were proved to exist spectrophotometrically, and similar ions were postulated to explain transference data in the case of uranyl chloride. The stability as a function of the solvent composition of the UO_2X^+ type of ion was found to be parallel in a remarkable way, with the logarithm of the specific velocity constant of the electron exchange reaction as a function of the solvent composition in the water-ethanol solvent system. If the data on ion complex stability to the kinetic situation are extrapolated, it would appear that the effect of the solvent on the stability of the UO_2X^+ complex is a principal factor in the influence of the solvent on the rate of the electron exchange reaction between $U^{(IV)}$ and $U^{(VI)}$ ions.

Solubility of Metallic Mercury in Organic Solvents. E. H. Klehr and A. F. Voigt, Ames Laboratory, Iowa State University, Ames, Iowa, U.S.A.

The solubility of metallic mercury at 25°C in the solvents carbon tetrachloride, 2,2,4 trimethylpentane, *n*-decane, benzene, toluene, nitrobenzene, chlorobenzene and bromobenzene has been determined by the use of Hg^{203} tracer. For all but nitrobenzene, measurements were made directly by shaking mercury metal of known specific activity with the pure liquid until equilibrium was reached. The value for nitrobenzene was calculated by measuring the distribution coefficient for mercury between the solvent and dilute aqueous acid and combining it with the measured solubility of mercury in the acid solution. For carbon tetrachloride, trimethylpentane and benzene both methods were used with good agreement. Measurements were made by counting precipitated samples with a Geiger-Müller counter or liquid aliquots with a well-type scintillation counter. Results were comparable but the latter method was more consistent. All solubilities were in the range (4·6 to 16) $\times 10^{-6}$ gram atoms/liter. For *n*-decane, toluene and chlorobenzene, the temperature dependence of the solubility was determined over the range 0 to 45°C.

The Hildebrand-Scott theory of solubility has been applied to these systems for comparison. For the aliphatic hydrocarbons, the values predicted by the theory are within 35% of the observed values. However, for the other solvents predicted solubilities are 4 to 18 times larger than observed. Reed's modification of the theory reduces the predicted values so that for most of the solvents they agree with the results within 30 to 100% but for trimethylpentane and *n*-decane they are low by a factor of 10. Part of the difficulty lies in obtaining exact values for the properties of the solvents used in calculating the predicted solubilities.

Curves of log C (solubility) vs. $1/T$ were straight lines with slopes similar to those obtained from the Hildebrand–Scott theory but displaced from those curves. These slopes were used to calculate the heats of solution for the three systems. Plots of log C vs. log T were used to calculate the entropies of solution by a method due to Hildebrand. This method gave values for ΔS at constant volume which were considerably higher than the ideal entropies of mixing at constant pressure. Correction to the same terms brought the two sets of values closer together but still not in good agreement. Possible reasons for the poor agreement are discussed.

Mass Dependence of Intermetallic Diffusion. D. Lazarus, Department of Physics, University of Illinois, Urbana, Illinois, U.S.A.

Studies have been undertaken to determine the specific effect of the isotopic mass on the rates of intermetallic diffusion, to test the application of absolute reaction rate theory to the diffusion process and the predictions of Bardeen and Herring regarding correlation between tracer and solvent atom jumps. Precision sectioning techniques are employed, using $iron^{55}$ and $iron^{59}$ tracers in pure silver and copper monocrystalline specimens. In order to measure the small mass dependence, extreme precision is required in the experiment. Since the two iron isotopes have completely different decay schemes, accurate differential counting can be performed using beryllium and gold absorbers, after a radiochemical separation of the tracers from the host material. Results indicat

that the relative rate of diffusion of the two isotopes is considerably less than that expected classically, implying either a departure from equilibrium during the elementary diffusion jump or a strong correlation between solute and solvent atom jumps. The temperature dependence of the effect is also discussed.

Radioactive Preparation of Defects in Solids. J. LAMBE, Physics Department, Ford Motor Company, Scientific Laboratory, Dearborn, Michigan, U.S.A.

One of the major areas of interest in solid state physics is the study of defects in nearly perfect crystals. The controlled formation of such defects is thus an important aspect of these studies. Chemical additions and radiation damage are among the techniques which have been widely used to make such defects. In the present work some possibilities have been examined of using radioactive decay to form defects in solids. The technique is simply to make as perfect a material as possible but with some of the host crystal atoms radioactive. When these atoms decay the daughter product essentially forms the defect. As a simple means of testing the feasibility of this technique, it was used to prepare tritium atoms trapped in a crystal of solid molecular tritium. In this method molecular tritium is frozen in a container as a small crystal of tritium or in a noble gas matrix. When one of the atoms of a tritium molecule decays, it becomes He^3, leaving behind the other atoms of tritium. This atom can then be studied by conventional techniques of paramagnetic resonance. In our experiment, one cc at STP of tritium gas was used. This is 2·6 curies. The tritium emits a weak beta particle which is easily shielded. This amount was frozen out in a quartz tube at 4·2°K. This amount of tritium will produce about 10^{11} atoms/sec. It required about five minutes to begin measurements, at which time one should have 3×10^{13} spins. Two main hyperfine lines are observed with a separation of 542 gauss as one would expect for tritium. This signal increases steadily. The experiments indicate that the technique is feasible and should have particular application to the preparation of free radicals in organic materials which are fairly resistant to radiation damage.

The Use of Oxygen^{14} in the Study of Positron Polarization in a Fermi-type Transition. F. H. SCHMIDT, J. B. GERHART, J. H. HOPKINS, H. BICHSEL and J. STROTH, University of Washington, Seattle, Washington, U.S.A.

The short-lived radioisotope O^{14} has been in two experiments designed to determine the degree of polarization of the decay positrons. In the two component theory of beta decay, first proposed by Lee and Yang, the non-conservation of parity implies that positrons will have their spin angular momentum polarized in the direction of motion by an amount proportional to their velocity divided by the velocity of light. The proportionality constant depends upon the type of interaction responsible for the decay process. The properties of seventy-two second O^{14} are suitable for a test of certain aspects of the theory. O^{14} decays from a zero spin, even parity state to another zero spin, even parity excited state in N^{14}. Therefore, the decay is a pure Fermi-type. The O^{14} was produced by an N^{14} (p, n) reaction in the University of Washington 60-inch cyclotron by a continuous N_2 flow system. O_2 carrier gas was added to the N_2. After activation the gas passed through suitable filters to remove unwanted activities, and to combine the oxygen with hydrogen. The active water vapor was trapped at liquid N_2 temperature on a copper rod to form a strong ($\sim$10 mc) continuous source of 72-second O^{14}. Decay positrons were energy analysed in a small magnetic spectrometer. The longitudinal polarization of the positrons emerging from the spectrometer was studied by two methods. In the first the positrons impinged upon a plastic scintillator where some of them annihilated in flight. The more energetic annihilation quantum is circularly polarized in the same sense as that of the original positron. These gamma rays were Compton scattered from magnetized iron and detected in a NaI(Tl) scintillation counter. An asymmetry in the scattering cross-section with the direction of magnetization is related to the original amount of positron polarization. In the second method the positrons were focussed upon a magnetized iron foil. The positron-electron, or Bhabha, scattering cross-section depends upon the sense of magnetization of the iron foil relative to the positron polarization. The scattered electron and positron were detected in plastic scintillation counters operating in fast coincidence. For both methods the expected asymmetries are small, and long counting periods were required. The results show that 1 MeV-O^{14} positrons are right-handed polarized. The annihilation method gave the value $(0{\cdot}73 \pm 0{\cdot}17)$v/c; the Bhabha scattering method gave $(0{\cdot}97 \pm 0{\cdot}19)$v/c. The simplest theory predicts 1·00 v/c. It is believed that the Bhabha scattering method is the more reliable chiefly because the relation between asymmetry and polarization is easier to calculate.

Resonant Absorption and Scattering of Nuclear Gamma Radiation. G. J. PERLOW and S. S. HANNA, Argonne National Laboratory, Lemont, Illinois, U.S.A.

It has been demonstrated by Mossbauer that, under certain conditions, the emission and absorption

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of nuclear radiation can take place without recoil. It is therefore not necessary to produce an energy shift to obtain the resonant absorption and scattering of gamma rays. Moreover, the line broadening of resonant radiation is in this case usually negligible, and extremely high resolution can be achieved. This mechanism not only provides a simple means of studying the interaction of nuclei with electromagnetic radiation, but, of greater importance, it provides an extremely sensitive tool for the investigation of a large number of physical problems.

A very favourable case is obtained with the Fe^{57} nucleus which has a first excited state at $E = 14{\cdot}4$ kev formed by radioactive decay of Co-57. The lifetime of the state is $0{\cdot}1\ \mu$ sec which corresponds to $\Gamma = 4{\cdot}5 \times 10^{-9}$ ev and hence $\Gamma/E = 3 \times 10^{-13}$. Thus the resonant absorption is a very sensitive detector of the frequency change of electromagnet in radiation.

The resonant absorption in Fe^{57} has been studied in considerable detail. The strength of the absorption, the line shape, and line shift have all been observed as a function of temperature. The polarization of the radiation has been examined by means of experiments with magnetized sources and absorbers. The hyperfine spectrum of the resonant radiation has been analysed with and without polarization. These studies have led to an interpretation of the hyperfine structure in terms of the properties of the nuclear states and the hyperfine interaction in iron. The effect of an external magnetic field on the hyperfine structure has also been investigated.

The resonant absorption in Fe^{57} has been used to study the connexion between the time development of the decay of a nuclear state and the spectrum of the observed radiation. Detailed observations are made of the time spectrum of filtered resonance radiation for a variety of conditions.

Nuclear Orientation Experiments with Oriented U^{233}, U^{234}, U^{235} and Np^{237} Isotopes. L. D. Roberts, J. W. T. Dabbs and G. W. Parker, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

The electric quadrupole coupling in uranyl, UO_2^{++}, and in neptunyl, NpO_2^{++}, ions is quite large and permits nuclear orientation experiments to be performed with uranium and neptunium in the relatively high temperature region of 1 to 4° Kelvin and above. In the case of the neptunyl ion there is also a magnetic hyperfine structure coupling which may play an important role in orienting Np nuclei if the temperature is substantially below 1°K. In the salts, uranyl or neptunyl rubidium nitrate, the UO_2^{++} or NpO_2^{++} ions have their symmetry axes parallel to the crystalline c-axis. Thus, at low temperatures the nuclei are effectively oriented with respect to this axis. Using this method of nuclear orientation studies have been performed of the nature of alpha particle emission and of neutron fission relative to the axis of the oriented nuclear spin system. Assuming the quadrupole moment of the U and Np nuclei to be positive, theories of the electron configuration of the UO_2^{++} or NpO_2^{++} ions have indicated that the nuclear symmetry axis should tend to orient parallel to the crystalline c-axis. Following the picture of alpha emission of Hill and Wheeler one would further expect this emission to be predominant along the nuclear symmetry axis, and thus along the crystalline c-axis as the nuclei become oriented. Our experiments have demonstrated that the predominant alpha emission is, in fact, perpendicular to the crystalline c-axis contrary to the above theory. On the basis of available information it seems likely that the picture of the chemical bond assumed above is in error.

Studies also have been performed on the angular distribution of fission fragments from the thermal neutron fission of oriented U^{233} and U^{235} nuclei. It is found that the fragment emission from U^{233} is isotropic and independent of nuclear orientation. For U^{235} the predominant fragment emission is along the crystalline c-axis when the nuclei are oriented. These results are discussed in terms of a picture of fission proposed by Bohr.

Meteorites as Space Probes for Cosmic Rays. O. A. Schaeffer, R. W. Stoenner and R. Davis, Jr., Chemistry Department, Brookhaven National Laboratory, Upton, L.I., New York, U.S.A.

An experiment has been performed to test the spatial constancy of high energy cosmic radiation within the solar system by measuring a short-lived and a long-lived cosmic ray-induced radioactivity in a recently fallen meteorite. This test depends on the fact that meteorites have highly eccentric orbits and therefore serve as space probes over the region between the earth's orbit and the asteroidal belt. The short-lived activity is produced while the meteorite is in the vicinity of the earth's orbit, while the ions long-lived activity is produced over the entire orbit of the meteorite.

The measurement was performed on the Hamlet chondrite that fell in Indiana on October 13, 1959. The 35-day argon-37 and the 260-year argon-39 activities were observed in the meteorite. The argon-37 and argon-39 activities found, corrected to the day of fall, were 19 ± 2 and 11 ± 2 dis/day/gram of meteorite. The relative amounts of these activities are to be compared to the production rates of these isotopes derived from bombarding a sample of the meteorite with 3 beV protons.

The argon-19 activity was measured in three other stone meteorites of known date of fall. The activities in dis/min/gram meteorite were as follows: Benton chondrite (1949), 10·6 ± 2·0; Richardton chondrite (1918), 10·8 ± 2·0; and the carbonaceous chondrite Murray (1955), 13·8 ± 2·0. From the mass spectrometric determination of the rare gases in these meteorites it is possible to derive the length of time the meteorites have been in space exposed to cosmic rays.

Radioactive Rare Earths from Fallout for a Study of Particle Movement in the Sea. THOMAS T. SUGIHARA, Clark University, Worcester, Massachusetts, U.S.A. and VAUGHAN T. BOWEN, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, U.S.A.

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As part of an extensive study of the distribution of long-lived radio-nuclides from fall-out in the Atlantic Ocean, a large number of measurements of concentration of cerium-144 and promethium-147 have been made. Comparison of these concentrations as they vary both horizontally and vertically, with simultaneously measured concentrations of strontium-90, and occasionally of caesium-137 indicates that the rare earths are generally depleted in surface water, by comparison with the nuclides known to be soluble. This observation, coupled with frequent observation of rare-earth enrichment at depth, leads us to postulate rapid vertical transport of rare earths by attachment to particles undergoing sedimentation. This is completely plausible in terms of the "radio-colloid" behaviour generally observed for rare earths at sea-water pH.

Analyses now in progress on collections of plankton organisms and on deep water samples from areas known to be fed by subsidence should permit reporting some rough estimates of the rate of sinking at various typical oceanic stations, and of the significance of biological processes in this phenomenon. An attempt is made to interpret this study in the overall picture of the marine geochemistry of the trivalent cations, as well as to emphasize the unique and generally useful aspects of the fallout tracer experiment.

Application of Radioisotopes to Studies of Crystal Imperfections. R. L. SPROULL, M. MOSS and R. POHL, Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York, U.S.A.

Radioisotopes have been used in two important ways in studying imperfections in alkali halide crystals. The zone refining of the compounds has been monitored by addition of tracers, and segregation coefficients have been determined from such measurements. The other application has been to insert small concentrations of impurity ions into alkali halides in order to study the phonon scattering by such impurities or by the vacancies they introduce; these measurements are carried out at very low temperatures where the phonon mean free path is limited by lattice imperfections. The most commonly used radioisotope in this work has been Ca^{45}.

An Investigation of Automated Activation Analysis. WILLIAM E. KUYKENDALL, RICHARD E. WAINERDI, and Associates.

A major factor delaying the development of activation analysis as a routine analytical tool is the large number of sequential interdependent operations which are inherent to the technique. In addition to accelerating these operations, the use of high speed computers offers promise in enhancing the accuracy of activation analysis through the application of certain statistical tests to the data during computer handling which would not be feasible in manual data analysis.

Rapid mechanical sample preparation, irradiation and counting techniques are necessary to permit the accumulation of the input data for the computer if full advantage is to be taken of the computer's analytical data handling speed. The parameters which govern the design of these mechanical devices are of considerable importance in optimizing the automated activation analysis system. The activating radiation, counting system, multi-channel analyzer and computer may be varied in particular applications, but the basic system requirements remain similar. In the subject investigation, a reactor neutron source, an anti-coincidence gamma spectrometer, and an IBM 704 computer are being used as the activation analysis system.

The system sophistication necessary to perform automated activation analysis depends upon the extent of uncertainty in the sample composition, the nuclear properties of the activation targets and products, and the number of components present. The memory requirements of the computer are a function of the degree of uncertainty in sample composition and the number of components present. The nuclear properties of the activation targets and products (including natural abundances, activation cross-sections, gamma energy levels, and half-lives) govern the activation, detection and multiple counting requirements of the system. The fact that the computer considers the characteristic half-lives of the various isotopes in addition to the conventional consideration of characteristic gamma spectra in activation analysis enables the computer to identify more component isotopes in a given sample with

reduced prior chemical preparation, which further enhances the speed and accuracy of analysis.

A computer programme has been completed which will process the data from samples containing a large number of different elements, but to illustrate the speed of the data handling sequence, the data from a sample containing four component elements is processed in a matter of minutes, including the presentation of the qualitative and quantitative analysis of the sample, with the speed of the data processing limited primarily by the speed which the output printer can attain.

The Radiometric Analysis of Non-radioactive Materials by Chemical Exchange. D. J. CHLECK and C. A. ZIEGLER, Tracerlab, Inc., Waltham, Massachusetts, U.S.A.

The use of radioisotopes to measure the composition of different materials via chemical exchange within an instrument is described. The product of the reaction is a radioactive gas which is counted and serves as the indicator of measurement.

This method has been applied to a number of different liquids and gases for their specific and sensitive determination.

The chief limiting condition on sensitivity is imposed by the specific activity of the radiochemical component. Where high specific activities are available, sensitivity in terms of chemical quantity will be very great. The recent development of quinol-krypton^{85} clathrate compounds has provided a basic radiochemical source which not only provides high specific activities at low cost but also excellent half life and energy characteristics.

These clathrate compounds can be oxidized only by very strong oxidizing agents, such as ozone to release Kr^{85}. When coupled with a salt, such as sodium chlorite, the sensing of other materials such as SO_2 may be accomplished. This reaction proceeds via a double chemical release:

$$SO_2(g) + ClO_2(s) \rightarrow ClO_2(g)$$

$$ClO_2(g) + 3\ \text{Quinol}\cdot Kr^{85}(s) \rightarrow Kr^{85}(g).$$

In this manner specific and sensitive determinations are obtained with reducing agents since the first gaseous reaction product is a powerful oxidizing gas.

Two applications of the radiometric technique employing clathrates are described. The first is the development of a balloon-borne sonde for the meteorological analysis of ozone in the upper atmosphere. The other is its use in air pollution and process control work in the form of a portable analyser. Different gases may be analysed by this device by merely changing the radio-chemical reaction cell.

Design and Characteristics of Beta-Excited X-ray Sources. I. FILOSOFO, L. REIFFEL, C. A. STONE and L. VOYVODIC, Physics Division, Armour Research Foundation, Chicago, Illinois, U.S.A.

The paper reports on recent work on beta-excited X-ray sources. Results of a detailed experimental investigation on the X-rays produced by the fission products Pm^{147}, Kr^{85} and Sr^{90} are described. X-ray yields and spectral distributions have been studied for target materials ranging from copper to uranium and in a variety of source-target geometries:

(a) transmission target, where the target is between the source and the X-ray detector
(b) reflection target, where the detector is facing the target surface struck by the beta rays
(c) sandwich target, with the target material on both sides of the beta source
(d) intimate source-target mixtures.

The mixture of Pm^{147} with samarium oxide has been investigated in particular detail to anticipate the performance of a high level source where the Pm^{147} itself represents the main X-ray target.

X-rays were detected using scintillation and proportional counters in conjunction with a 256 channel pulseheight analyser.

To interpret the experimental results, an analytical treatment of the processes involved in X-ray production by beta particles has been developed and is outlined. By taking into account bremsstrahlung, K-shell ionization, and fluorescent X-ray excitation, a convenient mathematical formulation may be derived for photon spectra and yields as functions of maximum β energy, target thickness and source configuration.

The agreement between calculated and experimentally determined yields is excellent and confirms the merit of the analysis. It thus becomes possible to optimize the design of isotopic X-ray sources for specific applications.

Kr^{85} and Pm^{147} prototype sources have been designed and their performance in thickness and composition analysis measurements is discussed. A high level Pm^{147} source for industrial radiography has also been designed and its performance, along with the utility of image intensifiers to extend its applicability, is considered.

A general review of potentialities, advantages and limitations of isotopic X-ray sources is given and selection of source design and detection method for optimal performance in a variety of current and future technical applications is discussed.

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Radiometric Chemical Analysis. A. G. SCHRODT, Detector Development and Chemistry, Nuclear-Chicago Corporation, Des Plaines, Illinois, U.S.A.

The radiometric method of analysis is noted for its sensitivity and its simplicity in both apparatus and procedure. A few inexpensive radioactive reagents permit the analysis of a wide variety of chemical elements and compounds. Any particular procedure is generally applicable over a very wide range of concentrations. The broad utility and adaptability of the radiometric method is evidenced by applications ranging from air pollution studies to automatic chemical process control. It is potentially an analytical method of great industrial significance.

Specific examples of analyses are cited to illustrate the capabilities of ordinary equipment. Apparatus specifically designed for radiometric chemistry may shorten the time required, and increase precision and accuracy for routine analyses.

Gas samples may be processed with continuous flow apparatus as in sulphur dioxide and ozone air pollution analyses. They may also be processed within sealed high vacuum systems.

Liquid and solid samples may be processed with special extraction, filtration or centrifugation techniques. These samples may be assayed most conveniently using a cylindrical thin wall flow type geiger counter or a well type scintillation counter.

A sensitive and convenient apparatus for the routine performance of radiometric chemical analysis is a special type of centrifuge which has been used in obtaining the data presented in this paper. This centrifuge consists of a stainless steel cylinder which spins at 3,500 revolutions per minute around a cylindrical thin wall flow type geiger counter. The reaction mixture is fed into this centrifuge while it is spinning. The precipitate is thrown to the wall with the supernatant solution covering it to a thickness infinite for the betas emitted by the radioisotope. The radioactivity of the solution is measured while the centrifuge is spinning. This device has been used as the basis for an automatic analyzer for phosphate ion programmed to follow a sequence of unknown sampling, reagent mixing, centrifugation, counting data presentation, and phosphate replenishment. This analyser can repeatedly measure phosphate concentration in the range of 5 to 50 parts per million with an accuracy of $\pm 5\%$.

Analyses by the radiometric chemical method are currently being devised for nearly half of all the elements in the periodic table. The paper reports the range of concentrations of reagents and unknowns which can be used as well as the limits of sensitivity for these analyses using the laboratory model of the centrifuge-detector. This information together with specifications of the apparatus parameters being determined will provide a basis for future design of radiometric chemical process control instrumentation.

Research Applications of Beta Particle Techniques: Back-scattering and X-ray Excitation. R. H. MÜLLER, Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico, U.S.A.

Studies in this Laboratory during the past seven years have established precise relationships for the backscattering of beta particles and these methods have been supplemented by techniques using isotope excited X-rays.

X-rays, so excited, have received wide attention throughout the world and in many cases have revolutionized industrial gauging practices.

This report is concerned with applications to precise absorptiometry, thickness of films, the identification and quantitative estimation of substances by absorption edge measurements, and to paper chromatography. In the latter, chromatograms can be evaluated by beta absorption, by X-ray absorption, or by excitation of X-rays in the various zones by beta bombardment. These alternative approaches are compared and evaluated.

Several microchemical techniques have been examined, and, either by beta absorption or by beta excitation of X-rays, small amounts of substances can be identified and determined. The lower limits of detection are not as small as one can achieve by tracer techniques, but there are numerous advantages, the primary one being that one deals with sealed sources from which contamination is virtually impossible.

For all these phenomena precise equations have been developed from the data—some empirical, and others substantially fundamental. It is interesting that these equations accurately predict optimum source parameters as established by other investigators here and abroad.

It is believed that these techniques confirm the opinion that radioactive isotopes have tremendous scientific and technical promise. As far as X-ray sources are concerned, it may be said that everything in X-ray technology, other than crystal structure elucidation, can be done more simply by these means. With multi-Curie sources, even the latter may eventually be possible.

New Processing Techniques for Radioisotopes at Oak Ridge National Laboratory. I. A. BUTLER, E. LAMB and A. F. RUPP, U.S.A.

Recent developments in the radioisotope production programme at Oak Ridge National Laboratory

include new processes and process improvements for the production of Cerium-144, Promethium-147, Calcium-47, Technetium-99, and Strontium-90.

Cerium-144 has been produced in kilocurie quantities in a test run. The Cerium-144 was separated from a fission product rare earth mixture by extracting into DI(2-Ethyl Hexyl) Phosphoric acid. A product recovery of greater than 98 per cent with a product purity of greater than 99 was attained. The cerium was further processed to obtain pure Cerium-144 oxide powder having an activity concentration of 193 curies per gram. The powder was pressed into pellets which were sintered to a dense ceramic form.

Promethium-147 has been produced in kilocurie quantities by a combination of precipitation and ion exchange techniques. A solvent extraction system for separating Promethium-147 from other rare earths has been tested on a tracer scale. Sintered pellets of Promethium oxide were fabricated from the Promethium-147 product.

The separation and purification of Strontium-90 from gross contaminants by a continuous solvent extraction flowsheet has been demonstrated on a tracer scale. Product quality of 98 per cent Strontium has been achieved from feed containing 95 per cent inert calcium contaminant. The Strontium-90 is further processed to form Strontium titanate ceramic elements.

Gram quantities of Technetium-99 have been recovered from fission product waste streams by a combination of precipitation and solvent extraction processes. The Technetium product was produced with a chemical purity of greater than 98 per cent and radiochemical purity of greater than 99.9 per cent.

Calcium-47 has been produced regularly in millicurie quantities by neutron activation of targets enriched in Calcium-46 by electromagnetic separation.

High Dilution On-stream Isotopic Tracer Techniques. A. F. Findeis, M. Vestal and W. H. Johnston, William H. Johnston Laboratories, Inc., Baltimore, Maryland, U.S.A.

The present paper concerns large scale tracer applications in which isotope tagging is done on a component of main flowing fluid or stream without subsequent mainline separation. The tagging includes radiotracers and stable activation tracers. Motivations are research information and control. High dilution uses which include tracing pollutants in rivers, waters in aquifers, and components of industrial process streams, require low-level counting methods.

Equations are derived which relate the required levels of tracer concentrations, the instrumental background, the efficiency of the detector, the required statistical reliability, the time desired for the measurements of sample and background, the stream flow rates, and the tracer nuclide. These equations are shown graphically and allow a ready selection of the tracer concentrations for specific applications.

The sampling programme for large scale tracer applications is analyzed for steady state and pulse injections. In the latter case, the longitudinal mixing is treated by the concept of eddy diffusion coefficients. By estimating certain parameters, the longitudinal tracer detection range and the first arrival time are obtained as a function of distance between injection and collection. A sampling programme giving start and stop collection times is indicated which insures that a minimum of seven samples containing detectable tracer concentrations is obtained.

For high dilution on-stream radiotracing with beta emitters, the detectors are large low-level internal gas tube counters, foil-flow counters, and plastic scintillators. These are compared and some new designs are described with experimental results. Two new anticoincidence counters are presented. The advantages of low atomic number shielding are emphasized. Experimental results with water containing a neutron absorber are given. The minimum backgrounds of these systems are summarized. For gamma emitters specialized large liquid and plastic scintillators for pipe flow systems are described and compared.

Recent developments in stable transistorized electronics for low-level counting are shown. A new amplifier and a new tunnel diode adder circuit are described.

For stable activation tracers, isotope neutron sources, pulsed neutron generators, and nuclear reactors are compared.

Examples are given of several new applications of high dilution on-stream tracers to problems of source identification of pollutions in rivers and streams.

Pulsed Neutron Source Applications to Radiochemistry. B. J. Carr, Kaman Nuclear, Colorado Springs, Colorado, U.S.A.

This paper describes the characteristics of several positive ion accelerators which operate on a pulsed basis and utilize the $T(d, n)He^4$ reaction to produce 14 MeV neutrons.

The basic difference between these accelerators and those referred to as Van de Graaff and Cockroft-Walton equipment is that both the ion source and accelerator are pulsed simultaneously to produce

extremely high source currents. In addition, these new, small accelerators require no vacuum equipment for proper operation.

The small neutron sources developed have been applied to numerous radiochemistry problems. For example, percentage of oxygen in beryllium oxide has been industrially analyzed. By counting between high intensity pulses the flux requirements for a fixed percentage accuracy in radiochemical analysis are lowered. This analytical technique is discussed in detail.

This technique simplifies the analysis of many short half-lived elements. Applications of the accelerators to oil well logging is also discussed.

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Separation of Tritium from Hydrogen by Thermal Diffusion. A. C. Briemeister, B. B. McInteer, R. M. Potter and E. S. Robinson, Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico, U.S.A.

In many of the applications of tritium a high degree of isotopic purity is necessary. The tritium obtained from neutron irradiation of lithium has associated with it varying amounts of hydrogen. Because of the large ratio of the masses of hydrogen and tritium, the highest possible between isotopes, almost any separation system will give a large enrichment. Details of a thermal diffusion column to produce large amounts of 99·8% T_2, routinely, are given.

Two separation methods have been used. The first method, diffusion of the gas through streaming mercury vapour (the Hertz Pump), was used when the tritium supply was scarce. Sixteen of these pumps were connected in series and tritium of high purity (99·7%) was drawn off continuously at a rate of 100 ml per day.

In 1950 when the supply of tritium increased, a hot wire thermal diffusion column was built. This system produced 10 litres of 99·8% tritium per day from 90% feed gas. In the construction of this system several problems arose due to the radioactivity of the tritium. One was the interaction of the radiation on various materials in the system, and the other was the continual growth of He^3. The use of neoprene in valves and gaskets was found to be acceptable if they were changed regularly. Special handling techniques were developed to pump, monitor and analyze the process gases without exposing the operating personnel to dangerous amounts of radiation.

The He^3 was periodically stripped from the tritium by differential adsorption on charcoal at liquid nitrogen temperatures. Care was taken to quantitatively save this material because of its scientific value.

The Use of Radiotracer Techniques to Study Lubrication and Wear in Large Diesel Engines. J. E. Howes, Jr., W. J. Braun and D. N. Sunderman, Battelle Memorial Institute, Columbus, Ohio, U.S.A.

Radiotracer techniques have been applied to the study of lubrication and wear in large diesel engines on a scale not before considered practical with perfect safety and with unique technological results. Both lubricating-oil consumption and cylinder-liner wear have been evaluated as a function of operating conditions on diesel engines in the 1000 BHP range. Techniques were developed for tapping 200 gal of lubricating oil with 60 millicuries of zinc-65 and determining oil consumption by exhaust gas sampling during operation under a variety of conditions. Measurement of the rate of lube-oil consumption could be made in 10 min rather than 24 to 48 hr required previously.

Irradiation techniques were developed for neutron activation of the lower cylinder portion of a 48-in. long, 8-in.-diameter cylinder liner. Suitable thermal-neutron shielding allowed production of 300-day manganese-54 which resulted in extending the useful life of the liner for wear studies by a factor of six to eight over that of a comparable liner thermally activated to produce iron-59.

The fact that studies with such large quantities of radioactive material can be carried out in standard research facilities in the diesel engine field opens an entirely new area to tracer applications. Selective activation and judicious use of thermal-neutron shielding increases the versatility of the tracer technique in localizing measurement to areas of interest, reducing the total quantity of radioactive material required in wear studies of large parts, and facilitating simultaneous wear measurement on engine parts of identical chemical composition.

Extension of the Techniques for Accelerated Unspecific Isotopic Labelling of Organic Compounds. N. A. Ghanem (on an IAEA fellowship from the United Arab Republic) and T. Westermark, Kungl Tekniska Högskolan, Stockholm, Sweden

The paper aims at reviewing new means of obtaining acceleration in the reaction of a radioactive gas with a target material to be labelled and examples of successful cases.

The techniques include the use of microwave and radio wave discharges, glow discharges affected through d.c. or a.c. sources, and simply ultraviolet radiation. The materials undergoing labelling covered a wide range of physical and chemical properties (from volatile and highly reactive ethylene

oxide to solid stable polystyrene). Specific activities of as high as 100 mC/g in purified significant quantities of products were obtained. Periods of exposure to discharge were of the order of one minute and decomposition was very limited in many cases.

Calculation of efficiency of the energy applied for production of labelling in these methods and in comparison with energy from ionizing radiation for the same purpose (Wilzbach, Doreman, and Lemmon), and of G values for isotope replacement are given. In polystyrene labelling, there is evidence that the mechanism is governed by an atom-molecule reaction. Although tritium was the main isotope used, the technique could be generalized to accelerating certain reactions with other radionuclides such as C^{14} and S^{35} (in $^{14}CO_2$ and $^{35}SO_2$ respectively) to produce high specific activity tracers.

The technique—especially regarding the microwave and glow discharges by 50 hz alternating current—is distinguished by being simple, time and material saving. Already many labelled compounds have been produced to serve useful purposes in Swedish industry and research. Many other areas seem to be open to new applications, e.g. the cellulose field. In other cases more safe use of isotopes seem possible e.g. static elimination.

Certain extension of tritium determination methods have been found such as the use of bremsstrahlung and liquid scintillation with d.c. photomultiplier measurements.

On the Production of Be^7 in the NRX Reactor by the $Li^7(p, n)Be^7$, $B^{10}(p, a)Be^7$, $Li^6(d, n)Be^7$ and $Be^9(n, 3n)Be^7$ Reactions. J.-C. Roy, Atomic Energy of Canada Ltd., Chalk River, Ontario, Canada

Beryllium-7 is an excellent nuclide for the study of different types of nuclear reactions induced by fast neutrons in a reactor. Some of the reactions could produce usable amounts of Be^7 in a reactor. Four different reactions have been observed to yield Be^7 in the NRX reactor. They are:

$$Li^7(p, n)Be^7$$
$$B^{10}(p, a)Be^7$$
$$Li^6(d, n)Be^7$$
$$Be^9(n, 3n)Be^7$$

The (p, a) reaction was initiated by recoil protons from neutron irradiation of boric acid. The (p, n) and (d, n) reactions were induced either by the recoil protons and deuterons from neutron irradiation of LiOH and LiOD targets or by protons and deuterons produced by (n, p) and (n, d) reactions on lithium or other target elements chemically combined with lithium.

The observation of the $Be^9(n, 3n)Be^7$ shows that there are neutrons in the NRX reactor with an energy greater than 23 MeV.

One of the reactions studied in the present work could be used to produce Be^7 in a reactor in places where cyclotron irradiations are not easily available. It is the $Li^7(p, n)$ reaction induced by recoil protons using LiOH as the target; for a fission neutron flux of 2×10^{11} n/cm^2-sec, 1 gramme of LiOH irradiated for 20 days would yield several microcuries of Be^7.

Isotopic Data to Study the Mechanism of the Oxidation of Mercaptoacetic Acid. D. Gál and L. Guczi, Central Isotope Laboratory, University of Szeged, Szeged, Hungary and Department of Radiology, Elelmiszeripari Kutató Intézet, Budapest, Hungary

Numerous researchers have been studying the autoxidation of compounds containing a mercapto group by molecular oxygen in the liquid phase. It has been stated that, in the course of the reaction, sulphide is formed, but the exact mechanism of this process has not been determined.

The oxidation of mercaptoacetic acid, at 50° and at a pH of 8, was investigated both in the presence of komplexon[IV] and in the presence of iron.

Na_2S, labelled with S^{35}, was introduced into the system and it was determined that the Na_2S increases, considerably, the rate of the oxygen uptake in both the processes catalysed by iron and free of iron ions.

In the course of the reaction the concentration of the sulphide, its specific activity and its total activity, were measured. In using these data and on the basis of the kinetic isotopic method, developed by Neiman and co-workers, it was possible to calculate the rate of the sulphide formation and of its further oxidation.

In comparing these data with other kinetic ones, it is shown that the oxidation of mercaptoacetic acid in the liquid phase is a branching chain reaction; one of its principal chains being formed by the formation of Na_2S and by its further oxidation. Moreover, it was determined that sulphate is formed in the course of the reaction only through the inorganic sulphide. Iron has catalysed the formation of organic disulphide and therefore it also has an influence on the sulphide formation.

Investigation of the Storage Capacity of Silver–zinc Batteries Using Radioactive Tracers. Tivadar Palágyi, Magyar Tudományos Akadémia Kémiai Kutató Intézet, Budapest, Hungary

According to the literature, the shelf life of silver-zinc storage batteries is not influenced by whether it is in a charged or discharged state during storage.

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This statement is in contradiction to the results obtained during investigations on the cell mechanism. To decide the question, radioactive tracer experiments were performed, with cells manufactured in the laboratory, having a nominal capacity of 10 amp-hr. In every case one labelled electrode was built into the middle of the cell.

It was assumed that a conclusion concerning the more advantageous storage method could be drawn from the contamination with the isotope of the electrodes of the cells stored in charged and discharged condition, respectively. Altogether 32 cells were built; 16 cells with a negative electrode labelled with Zn^{65} and 16 cells with a positive electrode labelled with Ag^{110}. Both isotopes were electrolytically deposited on the electrodes. After filling the cells with electrolyte and after 3 charging and discharging processes, eight cells from each of the Zn^{65} and Ag^{110} labelled groups were stored in a charged and eight in a discharged state. From each of the resulting four cell groups two cells were opened after one month's storage and two cells were opened after two, three and six month's storage, respectively. The activity of the electrodes was measured with a cylindrical G-M tube and the electrodes were replaced into the casing with the order unchanged. After the reassembly and filling of the cell with fresh electrolyte, the cycling for determining the cell life was started.

Experiments proved that while storing cells with a labelled negative electrode, both the positive and negative electrodes dissolve to a certain degree. The unlabelled electrodes of cells stored in a charged state were contaminated in a higher degree and, after storage, these cells yielded less cycles than the cells stored in a discharged state. From this fact, it can be inferred that storage in the discharged state is more favourable than in the charged state.

Contributions to the Solvent Effect in Isotope Exchange Reaction. E. KŐRÖS, E. SCHULEK and L. PATAKI, Institute of Inorganic and Analytical Chemistry, L. Eötvös University, Budapest, Hungary

The effect of solvent on the exchange rate and the possible ways of accelerating the studied exchange reaction, at constant temperature and concentration was investigated.

The exchange of iodine atoms between 1-phenyl-2,3-dimethyl-4-iodopyrazolone (4-iodo-antipyrine) and elementary iodine was chosen as a model reaction. Namely, I-antipyrine is soluble in most of the solvents, its iodine on C-4 is of a rather nucleophilic nature, and it can be expected that, owing to the dissociation of I^+ ions, the exchange rate will increase in polar solvents.

First the effect of the dielectric constant [ϵ] was examined. It appears that the rate of exchange is affected not solely by ϵ. The structure of the solvent, and the micro-conditions prevailing in the single spatial particles of the solvents also play an important role.

The rate of exchange was also studied in a homologous series. In addition, the effect of the water content of the solvents was examined. The results show that there is a possibility of measuring the concentration of solvents, which encourage a quick exchange, in solvents where the exchange is slow. Investigations are in progress.

Exchange was also studied in aromatic solvents and the effect of the substituents is discussed.

Solvent	$t_{1/2}$
Benzene	32 m
Toluene	18 m
Chlorobenzene	11 m
Nitrobenzene	<20 s

Further, the exchange reaction was carried out in the presence of compounds which promote the heterolytic dissociation of iodine (such as $HgCl_2$, $AgNO_3$).

The exchange reaction carried out in the presence of $AgNO_3$ showed the mechanism of the reaction $Ag^+ - I_2$ to be as follows:

First step: $Ag^+ + I_2 = AgI + I^+$

I^+-ions quickly disproportionate:

$$3I^+ + 3H_2O = 2I^- + 10_3^- + 6H^+.$$

However, the exchange reaction of I^+ ions with I-antipyrine is faster.

No exchange was found between IO_3^- and I-antipyrine, and the exchange between I^- and I-antipyrine is extremely slow ($t_{1/2} \cong 2d$).

The important role of I^+ ions in the exchange reaction is dealt with. Also the possibility is pointed out of demonstrating the intermediate formation of I^+-ion in certain chemical reactions.

The exchange reactions between I-antipyrine and OI^-, ICN and I_3^- were also studied and discussed.

Preparation of C^{14} Labelled Tetrazolium Salts/TTC, NT, BT/and Tracer Study of the Tetrazene-formazan Rearrangement. J. MÁRTON, Magyar Tudományos Akadémia Kémiai Kutató Intézet, Budapest, Hungary

Tetrazolium salts form an important group of reagents of biochemical interest. In spite of this fact C^{14} labelled tetrazolium salts have not been prepared

hitherto. So far only a I^{131} labelled tetrazolium salt has been reported in the literature.

The preparation of (5-C^{14})-TTC, (5,5′-di-C^{14}) NT (neotetrazolium) and (5,5′-di-C^{14})-BT (tetrazolium blue) starting from benzaldehyde-(1-C^{14}) has been accomplished. The yields for both mono- and ditetrazolium salts are sufficiently high and the products can be obtained with high specific activity.

The purity of the samples was investigated by paper chromatography. In the case of ditetrazolium salts some impurities could be detected and conclusions drawn to as their structure and quantity. A method has been developed to prepare C^{14} labelled ditetrazolium salts of high purity.

The formation of the formazan, the precursor of the tetrazolium salt, goes through an unstable intermediate of tetrazene type structure which rearranges rapidly in basic medium, giving the formazan. The tetrazene intermediate can be isolated under suitable conditions. By using C^{14} labelled benzaldehyde phenylhydrazone this rearrangement was investigated and a verification of its intramolecular character given.

By using C^{14} labelled tetrazolium salts a new sensitive method has been developed for the estimation of corticosteroids in quantities of 0,01 μg. Estimations of other reducing substances (e.g. sugars, ascorbic acid etc. . . .) are in course.

A General Method for the Preparation of C^{14} Labelled Isocyanates and Isothiocyanates. Tracer Study of the Dimerization of Isocyanates. L. Ötvös, J. Márton and Mrs. J. Meisel, Magyar Tudományos Akadémia Kémiai Kutató Intézet, Budapest, Hungary

The tendency of isocyanates to dimerize in the presence of suitable catalysts and the thermal dissociation of the formed dimers has been known for a long time. Recently, an exchange equilibrium between isocyanates and isothiocyanates has been reported. It has been assumed that this exchange also takes place through the formation of a dimer.

The investigation of this exchange reaction with C^{14} as a tracer has been performed in order to establish the preparative usefulness of the reaction and to study its mechanism.

Phenyl-isocyanate-carbonyl-C^{14} has been prepared for this purpose by the Curtius reaction, on a semimicro scale.

This compound was equilibrated with inactive aryl isothiocyanates and alkyl isocyanates, respectively, after which a C^{14} labelled species of the originally inactive compound was isolated. The results showed that under suitable conditions this exchange reaction can be generally applied for preparing both C^{14} labelled isocyanates and isothiocyanates. As a side reaction the formation of polymers may occur. This was studied also as a function of temperature and time. A method has been developed for the preparation of labelled isocyanates with a good yield.

By studying the mechanism of the reaction both in the presence of and in the absence of catalysts, evidence is given for the occurrence of carbonyl groups exchange of isocyanates in both cases. Therefore the intermediate dimer must possess the structure of 1,3-diaryl-1,3-diaza-cyclobutane-2,4-di-on, suggested previously on the basis of crystallographic data. It has also been shown, that a series of another type of intermediates might occur during dimerisation and dissociation, and a general scheme is proposed for the mechanism of this reaction, involving possible intermediates, side reactions and products.

A New Method for the Preparation of I^{131}-labelled P-iodo-Benzene-sulfonic Acid Anhydride (Pipsan). N. H. Christensen, Atomenergikommissionen, Forsøgsanlaeg Risø, Roskilde, Denmark

I^{131}-labelled Pipsan may be used, together with S^{35}-labelled Pipsan, in a double isotope derivation technique for the analytical determination of various steroids.

The preparation of high specific activity I^{131}-Pipsan involves serious health hazards due to the γ-radiation of I^{131}, and a shielded cell with remote handling equipment has to be used. The previous method, in which I^{131} is introduced in diazobenzenesulfonic acid, involves many steps with purification of the intermediary products and necessitates rather complicated equipment.

By introducing I^{131} in diazo-benzene and by sulfonating the labelled iodobenzene with oleum, labelled Pipsan is obtained directly. This method has proved feasible for remote handling in a shielded cell. Chemical aspects of the procedure, which is based on recent Russian papers, are briefly discussed.

Descriptions are given of some of the equipment used in the remote handling, e.g.: a micro steam distillation apparatus for the preparation of iodobenzene, and a rotating perspex pipetting station used for the addition of washing liquids, for air-propagation and for the removal of supernatants.

Latitudinal Effect in the Transport of Radiocarbon from the Stratosphere to the Troposphere. H. Tauber, Carbon-14 Dating Laboratory, Dept. of Natural Sciences, Nationalmuseet, Copenhagen, Denmark

The large amount of bomb-produced carbon-14 (approximately 4 Megacuries), which has been

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released chiefly in the stratosphere, offers possibilities of investigating the routes of transport of carbon dioxide from the stratosphere to the troposphere, as well as the mixing times within the stratosphere and the troposphere. This is done by measuring the rates of increase in the C^{14} content of atmospheric CO_2 and of plant material. Such measurements are available from many different localities.

Carbon-14 measurements in Denmark on cereals have shown that during the years 1958 and 1959 the increase in C^{14} content was several per cent higher in this country than the average increase for the hemisphere. By the summer of 1959 the C^{14} content was 33 per cent above the 1954 level. The large increases in 1958 and 1959 are probably a C^{14} parallel to the spring peaks in Sr^{90} fall-out found in the North Temperate Zone in the same years.

The additional increase in the C^{14} content of Danish cereals above the average for the hemisphere suggests latitudinal variations in C^{14} contamination. This is in keeping with the findings for particulate fallout, which is brought down from the stratosphere by the same circulation mechanism. Latitudinal effects of this magnitude make it possible to track the routes of transport from the stratosphere to the troposphere by direct measurements of the C^{14} activity of tropospheric CO_2 from a number of widespread sampling stations.

Measurement of the Wear of Cast Grinding Balls Using Radioactive Tracers. J. D. KEYS and G. G. EICHHOLZ, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Ontario, Canada

The wear rate of grinding balls used in ball mills is usually hard to determine under operational conditions and little is known about the factors determining ball life. Radioactive tracers have been used successfully to mark cast steel balls to obtain information on their life under various operating conditions for comparison with balls of different type or composition. A batch of marked steel balls has been followed through a milling operation over several weeks and statistics on wear and loss of weight have been obtained.

In different test runs iron^{59} and cobalt^{60} were added to the molten metal prior to casting. The cast balls were then observed in use at an iron mine and a gold mine. The radioactive batch was added to a ball mill with a normal charge of about 85 tons and the mill charge was sampled at weekly intervals to pick out active balls. These balls were inspected and weighed, and the wear rate has been calculated. This procedure has proved to be a practical way of investigating wear properties under plant operating conditions.

Carbon Suboxide Labelling in a Radiation Field. M. A. ROLLIER, V. MAXIA and E. SPADACCINO, Istituto di Chimica Generale, University of Cagliari, Cagliari, Sardinia, Italy

The formation of C^{14} labelled carbon suboxide by isotopic exchange reaction between the labelled oxide and the inactive suboxide is investigated. High voltage discharge, X-rays and low intensity (about 10^5 $n/cm^2/sec$) reactor radiation (gamma rays + fast and slow neutrons) are used to improve the yields in order to get a high specific activity carbon suboxide to be used as starting material for the synthesis of carbon suboxide many organic derivatives.

Investigations of the Chemical States of Carrier-free Phosphorus^{32} as Extracted into Water from Pile-Irradiated Sulphur. J. B. DAHL and O. R. BIRKELUND, Institutt for Atomenergi, Kjeller, Lillestrøm, Norway

One of the methods of producing carrierfree phosphorus^{32} today is by extraction into water from pile-irradiated sulphur.

The present work gives information concerning the chemical states of phosphorus^{32} in aqueous solutions at different steps of the routine production process. The variation in the chemical state of phosphorus^{32} compounds in the final product has also been examined as a function of storage time.

Phosphorus^{32} bound as orthophosphate was found to be the main component. During the chemical processing the amount of orthophosphate increased from about 70% at the beginning of the extraction to about 98% in the final carrier-free phosphorus^{32} product.

The residual amount consisted of a mixture of pyro-, tri-, tetra-, and other long-chain polyphosphates (number of $P \geq 5$). No metaphosphates (ring-formed) were found in the solutions during production and storage.

The results indicate that the polyphosphorus compounds were formed in the target material during irradiation.

Special attention was paid to the adsorption of carrierfree phosphorus^{32} compounds to glassware under the existing experimental conditions.

At tracer concentrations of phosphorus^{32} in carrier-free solutions with pH ranging from 5 to 8, about 50–70% of the radioactivity was adsorbed within 7 days. At pH values below 5 and above 8 the adsorption effect was decreasing. Within 20 days less than 10% adsorption was observed in the pH interval 2–3. Characteristical adsorption curves were found for various glass qualities.

A similar adsorption effect was observed for phosphorus^{32} concentrations at millicurie level but the effect was not so pronounced.

The Use of Radioisotopes in Radiation Chemistry: The Effect of Radiation on Toluene*. K. E. WILZBACH, Argonne National Laboratory, Lemont, Illinois, U.S.A.

The radiation chemistry of organic compounds can often be studied more effectively and in greater detail using compounds labelled with radioisotopes. Use of this approach permits observation of products not otherwise detectable and provides information about the processes by which they are formed.

The versatility of this technique is illustrated by results obtained in a study of the radiation chemistry of toluene. Toluene labelled in the methyl group with tritium (one atom per 600 molecules) was prepared and was exposed in the vapor phase to gamma radiation (1 eV per molecule). The product was fractionated and the volatile fractions were injected into a gas fractometer equipped with an ionization chamber to permit simultaneous recording of radioactivity and thermal conductivity. Concentrations of tritium in the various products were determined from relative areas under peaks in the two curves.

The results are summarized in the following table, which presents the products observed, their "*G*" values, and their radioactivity.

Product	"*G*" value	Radioactivity (molecules/T atom)
Hydrogen	0·33	3000
Methane	0·11	600
Acetylene	0·45	4000
Ethylene	0·036	2000
Ethane	0·035	600
Benzene	0·10	4000
Ethylbenzene, *m,p*-Xylene	0·054	300
o-Xylene	0·009	300
Polymer	5	600

From the concentrations of tritium in these products it can be deduced that the methane is formed exclusively from the methyl group of toluene and that the xylenes are formed by attack of methyl radicals on toluene.

Oxidation of the recovered toluene showed that transfer of tritium from the methyl group to the benzene ring had occurred to some extent during the irradiation. The benzoic acid contained one tritium atom per 140,000 molecules, corresponding to a *G* value of 0·3 for the "exchange" reaction. This appearance of tritium in the ring could result either from abstraction of methyl hydrogen by a tolyl radical or from reconversion of a symmetrical intermediate, such as the tropylium ion*, to toluene. To provide information on this point the irradiation of toluene labelled with carbon^{14} is being investigated.

The fact that this interesting aspect of the radiation chemistry of toluene could not have been observed or investigated without the use of radioisotopes is patent evidence of their value as a tool in such studies.

Ion Exchange Studies of α-HydroxyCarboxylic Acid-lanthanide and Actinide Systems. G. R. CHOPPIN and D. MOY, Florida State University, Tallahassee, Florida, U.S.A., and L. W. HOLM, Försvarets Furskningsanstalt, Sundbyberg, Sweden

Alpha-hydroxy carboxylic acids have been used extensively for the separation of lanthanide and actinide elements with cation exchange resins. Sorption of these elements in the same solutions occurs on strong base anion exchange resins. A study has been made by elution and equilibrium distribution techniques of the behaviour at tracer level concentrations of these anion exchange systems. One objective was to measure the separation factors to assess anion exchange as a possible complement to cation exchange separation. Since very little attention has been given to characterizing the complexed species present in these separation systems, a second objective was to attempt through interpretation of both cation and anion exchange data such characterization.

Glycolic, lactic and α-hydroxy isobutyric acids were used over a concentration range of 0·01 to 1·0 M with Dowex-1 resin. The solutions were brought to a pH of 4·6 with NH_4OH. Radioactive tracers of Ce, Pm, Eu, Tb, Tm, Y, Cm and Cf were used in these studies. The elutions and equilibrium distributions were performed both at 25°C and 87°C.

In all three eluants the separation factors were smaller for the anion exchange than for the analogous cation exchange. In the glycolate solutions, the separation factors were largest and the values of the distribution coefficient K_D indicated that these were the most stable complexes.

The plots of log K_D vs. log anion concentration pass through a maximum then approach a slope of -1 indicating the presence of an anionic complex MX_4^-. The existence of this negative complex in the solution phase was demonstrated by electromigration studies of Tm-170 tracer in these solutions. At the solution concentration corresponding to the maximum K_D value, it can be shown that the predominant solution species is MX_3.

Approximate successive stability constants have been calculated for these systems and with these it is

* P. N. RYLANDER, S. MEYERSON and H. M. GRUBB *J. Amer. Chem. Soc.*, **79**, 842 (1957).

possible to construct diagrams showing the relative concentration of the species M^{+3}, MX^{+2}, MX_2^+, MX_3 and MX_4^- as a function of the concentration of X^-. It can also be proven from this data that the major mechanism for resin sorption is:

$$MX_3 + RX - - - - RMX_4.$$

Activation Analysis Utilizing Fast Radiochemical Separations and Portable Neutron Generators. W. W. MEINKE, Department of Chemistry, University of Michigan, Ann Arbor, Michigan, U.S.A.

Experience at the University of Michigan in adapting radiochemical procedures to short half-lived radioisotopes and in working with neutron generators indicates that activation analysis can become a rapid routine industrial method for certain types of analysis. Recently available portable neutron generators with thermal fluxes approaching 10^8 to 10^9 neutrons cm^{-2} sec^{-1} offer the large analytical laboratory its own source of neutrons for activation analysis at a cost of about $20,000. In addition, rapid radiochemical procedures permit separation of activated products in a matter of minutes and completion of analyses for many elements in less than an hour.

The pneumatic tube facilities of the Ford Nuclear Reactor at the University of Michigan deliver a sample to a hood three seconds after the end of irradiation and subsequently deliver a prepared counting sample to the detector in two additional seconds. Work with short lived radioisotopes is limited, therefore, only by the time required for radiochemical separations.

Rapid radiochemical separations have been devised for materials such as the 3·8-minute vanadium-52, 4·4-minute rhodium-104, 5·2-minute copper-66, 2·3-minute silver-108, 4·2-minute thallium-206, 5·8-minute titanium-51, 2·3-minute aluminium-28, 6·6-minute niobium-94, and 10·5-minute cobalt-60 min. The sensitivities obtained from a six minute irradiation of each of these elements are at least the same order of magnitude and often better than those obtained with lengthy irradiations. Typical separation time for vanadium is 4 minutes, for silver, 5 minutes. Thus it has been possible to make complete analysis of samples ranging from meteorites to rat liver tissue, from marine biological ashes to crude petroleum, all within periods of $\frac{1}{2}$ to 1 hour.

These fast radiochemical techniques are also being applied to an evaluation of a Texas Nuclear Corporation neutron generator for use in activation analysis. This Cockroft-Walton machine is small and compact; portable concrete shielding blocks suffice for protection. Optimum designs for shielding and moderator are being developed and will be described. Although the present flux obtainable is less than 0·1% of the flux available in the pneumatic tube positions of the Michigan reactor, it is still sufficient to determine microgram amounts of an element such as vanadium.

The Use of Radioisotopes in Studying Organic Reaction Mechanisms. A. P. WOLF, E. BAYSAL, C. S. REDVANLY, Chemistry Department, Brookhaven National Laboratory, Upton, L. I., New York, U.S.A.

The Disproportionation of Ethylbenzene under the Influence of Aluminium Bromide and Hydrogen Bromide.

Ethylbenzene will disproportionate in the presence of Al_2Br_6 and HBr at 0° in a series of rapid and reversible steps to give an equilibrium mixture of ethyl, diethyl and triethylbenzene. Second order kinetics have been observed for this reaction. A mechanism was proposed involving attack by ethyl benzene on the back side of the alkyl group of the corresponding *o* complex. Brown and Smoot in a further study of this system suggested that the large rate difference between toluene and ethylbenzene should be attributed to the prior formation of a π complex from the *o* complex. It was suggested that the equilibrium concentration of this π complex increases as one goes from toluene to ethylbenzene. The observed rate then depends on the concentration of the π complex and the rate at which it attacks another ethylbenzene.

The hypothesis of Brown and Smoot was tested by carrying out the reaction with ethylbenzene-1-C^{14}. The reaction was run so that final equilibrium was not attained. Ethyl benzene was isolated and degraded.

The degradative scheme allows the determination of activities in the ortho, meta and para positions by the solution of three simultaneous equations. In addition, internal checks in the system minimize the possibility of additive isotope effects.

The results indicate 42% rearrangement of the activity initially in the one position (100% of the activity was in the one position in the starting material) into the ortho, meta and para positions under our conditions. Further, the activity is greatest in the para position, lesser amounts being in the meta and ortho positions, in that order. The mechanistic postulates of McCauley and Lien and Brown and Smoot do not seem to be in accord with this result. Several reaction mechanisms consistent with the reported second order kinetics and the sequence of reactivities of alkyl benzenes will be suggested.

It remains to be shown that the observed activity redistribution in the ethyl benzene results from an

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intermediate involved in the disproportionation reaction rather than being the result of some other reaction not in the main reaction sequence.

Transmutation Doping and Recoil Effects in Semiconductors Exposed to Thermal Neutrons. J. M. CRAWFORD, JR. and J. W. CLELAND, Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee, U.S.A.

Nuclear reactions accompanying thermal neutron capture provide an effective means of introducing acceptor or donor impurity into certain semiconductors. Moreover, the fixed rate of radioactive decay permits time-dependent observations of electronic properties, e.g. the rate of shift of chemical potential with impurity introduction may be used to determine ionization energies of defects or impurities in much the same way as potentiometric titrations. Also nuclear doping permits compensation of existing acceptors or donors, thereby altering the concentration of charge carriers and provides a means of investigating the effect of impurity-compensation on carrier mobility and impurity-banding phenomena. Besides chemical impurity, lattice defects may be erected via recoil of nuclei on emission of radiation: capture γ-rays or decaying radiation.

Extensive studies of thermal neutron exposure of garmanium have been made. Of the five isotopes three transmute to chemical impurity whose yields in atoms per 100 neutron captures and half-lives are: Ca^{71}—30·4, 11·4 days; As^{75}—9·8, 82 min; Se^{77}—1·2, 39 hrs. Therefore, 3 acceptors (Ca^{71}) are introduced for each donor (As^{75} and Se^{77}) and through choice of exposure one may decrease the electron concentration of *n*-type Ge to very low values or convert n-type Ge to *p*-type. The half-life leading to Ca^{71} is conveniently long so that details of the "radioactive titration" may be followed by Hall coefficient and conductivity. Experiments also show that approximately one electron per neutron capture is removed by lattice defects created by the recoil of nuclei capture γ-ray emission. These displaced atoms may be restored to normal lattice sites by annealing at $-450°C$.

Recoil effects in silicon have also been observed, approximately two charge carriers being removed per capture. Implications of these results and those on germanium will be discussed in terms of the capture γ-ray spectra. In indium antimonide the capture γ-rays from In^{115} are not sufficient to displace a large number of nuclei and the major effect is production of Sn^{116}, a donor when substituted in an indium lattice position. Nuclear doping holds promise for investigating numerous compound semiconductors in which introduction of impurity by chemical means is difficult.

Survey Paper on Recent Advances in the Field of Recoil Chemistry. G. HARBOTTLE, Brookhaven National Laboratory, Upton, L.I., New York, U.S.A.

Recent work in Recoil Chemistry will be summarized and discussed. As important aids to furthering our knowledge of complex systems, the role of new techniques such as vapor-phase chromatography, ion exchange and paper electrophoresis will be emphasized. An attempt will be made to relate current work in Recoil Chemistry to other fields of investigation.

Adsorption Studies at Ionized Surface Layers by Means of Hot Atoms. M. AVRAHAMI and H. B. STEIGER, Department of Chemistry, Technion-Israel Institute of Technology, Haife, Israel

Adsorption of ions at the surface of solutions of ionic surface active substances can directly be studied using hot atoms. Extremely small amounts of suitable radioactive ions, or ions liable to undergo induced nuclear transformations *in situ*, are added to such solutions, replacing some of the normal counter ions co-adsorbed at the primary adsorbed organic ions. Hot atoms with energies from about 100 KeV down to a few electron volts give ranges in water from about 1000 Å down to monomolecular layers. This makes them suitable for sensitive surface layer studies. The hot atoms ejected from the surface are collected and counted.

Among α-disintegration recoils, the system Bi-212/Tl-208 had proved to be suitable.

Now, by refining the method valuable information about adsorption conditions at sodium dodecyl sulphate surface layers could be found. The kinetics of adsorption was studied by following in time the collected recoil activity caused by Bi-ion adsorption. Adsorption isotherms of Bi-ions as a function of the bulk concentration of the surface active substance under varying conditions of ionic strength, pH and Bi-212 activity were measured.

By comparing these isotherms with those obtained by measuring the surface tension of the solutions and calculating the surface excess with the aid of a suitably modified Gibbs' isotherm, the adsorption of Bi^{+++} and Pb^{++} relative to that of Na^+ and H_3O^+, and by this the extent of ion exchange in the adsorbed layer could be determined.

As the method measures the adsorption of charged species, surface reactions transforming primary adsorbed organic anions to a nonionic state could be followed. Conclusions about the formation of a non-ionized acid seep in the surface and about micelle formation in the bulk under various experimental conditions could be drawn.

β-disintegration recoils penetrate only few atomic layers. Their collected activity should indicate the thickness of the primary adsorbed layer, which depends on its state of condensation and orientation. Preliminary results about the penetration of β-recoils through such asdorption layers have been obtained.

Experiments applying radiative capture recoils for surface studies are under preparation.

The Use of Radioisotopes in Geophysics and Meteorology. L. Facy, World Meteorological Organization, Geneva, Switzerland

The use of radioisotopes in geophysics and meteorology may be viewed schematically in three different ways: as the main part of a measuring device in which the parameter to be measured causes variations of intensity of a standard source, as a tracer for observing the movements of a natural medium; as a dating element, or sometimes even as an indirect test for determining *a posteriori* temperatures of changes of state. As the last two applications may be simultaneous the radioisotope used can be either natural or artificial.

In the first part the author reviews the various meteorological and geophysical parameters that may be measured or traced by these various methods.

In the second part he enumerates, from reports submitted to the W.M.O. by member countries, work done and apparatuses devised in connexion with the use of radioisotopes.

Methods of Estimating the Operative Properties of Lubricating Oils with Radioactive Tracers. U. S. Zaslavsky and G. I. Shor, U.S.S.R.

The production of high-grade oils for modern propulsion units, machines and mechanisms depends to a great extent on the existence of effective laboratory methods for investigating and estimating their operative properties.

The high sensitivity of the radioactive tracer method makes it possible to devise rapid laboratory procedures for investigating the operative properties of oils with additives, and ascertaining how these act.

A tracer method was devised for investigating electrokinetic processes and sedimentation in oils with additives containing labelled carbon black. It employs beta counters acting both as radiation detectors and electrodes; these create an electric field, so that the displacement rate of the labelled carbon black in oils containing additives, under the influence of the electric and gravitational fields, can be recorded automatically. The method is suitable for investigating different dispersion systems with a labelled dispersal phase.

The authors define precisely the essential difference between the requirements for the chemical compounds respectively constituting anti-corrosive and anti-friction additives. That difference is the basis of a complex method of investigating multi-component additives having a high anti-friction efficiency but no corrosive action. The method employs radiometric determination of the corrosive effect of oils containing anti-friction additives during interaction with radioactive copper, selection of the most corrosive anti-friction components, choice of effective anti-corrosive components to go with these, and determination with the 4-ball apparatus of the anti-friction efficiency of the mixture so chosen.

The paper describes the results of measurement of the absorption and scattering of the beta radiation from different radioisotopes in sedimentary layers of varnish and scale. Methods were devised for investigating the cleansing properties of motor oils containing additives when used in laboratory equipment and propulsion units.

Laboratory investigation with radioactive tracers of the neutralizing properties of additives mixed with motor oil was used for determining the elimination of these properties when different constituents of additives were mixed in. The results of the laboratory investigations are compared with the data from engine tests.

Radioactive Apparatus for Measuring the Thickness of Hot Sheet Metal between 5 and 50 mm. B. N. Vasichev, V. K. Latyshev, U. S. Pliskin and A. K. Felinger, U.S.S.R.

Automation of the various mechanisms, and a single automation system linking all the rolling assemblies together, are necessary in order to make the dimensions of rolled metal more accurate and to improve the output of rolling equipment. The problem cannot, however, be solved satisfactorily without instruments for checking the thickness of the sheet during the rolling process.

These instruments must satisfy the following requirements:

1. measurement must be as fully automatic as possible;
2. measurement must be very accurate;
3. the instruments must work fast enough to keep pace with the rolling operations at all times;
4. the instruments must stand up to the rough conditions of metal rolling.

The instrument described in the paper measures the attenuation of gamma radiation after passage through the sheet under test. In order to achieve great precision of measurement under rolling conditions, a compensation method must be adopted.

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The authors chose a dynamic method of compensations, by which the comparison parameter moves through all the values in the range of measurement, whereas the zero component designates only the moment when the measured parameter and the comparison parameter are equal. This method eliminates the mechanical return communications and variable displacements of the static compensation method, and gives an instrument which is both sufficiently accurate and operates with sufficient speed in the complicated process of rolling.

The authors describe the basic design of the instrument, and discuss the factors affecting accuracy of measurement of a sheet (temperature, undulation, superficial moisture, composition of the sheet, and its position on the roller train).

The authors also describe the construction of an experimental instrument for industrial use over a thickness range of 14–44 mm.

The industrial tests carried out with the instrument showed that, with a Cs^{137} source of activity 9·2 g radium equivalent, the accuracy of measurement of the thickness of hot sheet within the specified range is $\pm 0{\cdot}1$ mm. The instrument's operating speed is one measurement per second. It works reliably under the conditions of the rolling mill.

Study with Radio-sulphur of the Kinetics of the Process $SO_2 + 0{\cdot}5O_2 = SO_3$ in a State of Chemical Equilibrium on a Platinum Catalyst. V. A. Roiter, N. A. Stukanovskaya and G. P. Korneichuk

The authors describe an attempt to use radioisotopes in the study of the kinetics of heterogeneous catalytic processes in a state of equilibrium. Selection of sequence patterns for the processes in conditions of equilibrium is bound to be governed by the limitations of thermodynamics. Current views on the catalytic mechanism, under normal conditions, of the processes here investigated can be critically examined, by comparing the laws of kinetics formulated in conditions of equilibrium with those formulated in the absence of equilibrium.

The investigation was carried out by the circulation method. After establishment of equilibrium, a small amount of $S^{35}O_2$ was introduced into the system as a tracer and its conversion rate into $S^{35}O_3$ was measured. From that rate the speed of the direct and inverse processes of oxidation of SO_2 on the catalyst was calculated. The equilibrium concentrations and temperature were varied. The results are satisfactorily expressed in the following equations: $W_1 = K_1 C_{SO_2} \cdot C_{O_2} 0{\cdot}5$ for the direct process, and $= W_2 K_2 C_{SO_3}$ for the inverse process. The same equations also express the kinetics of the process, measured by the usual circulation method in the absence of equilibrium (transformation rate $\chi = 70$–80%). The mechanism of the process is obviously the same under normal conditions as in a state of equilibrium: it must correspond to the principle of equilibrium of the individual parts. For this reason, patterns of mechanism which do not meet this requirement (e.g. semi-equilibrium, chain mechanism) should be ruled out. Possible sequence patterns for the process are suggested and discussed.

Although the kinetics are common to a state of equilibrium and to its absence, the absolute values of the velocity constants measured in a state of equilibrium are much lower, and the amount of heat required for activation ($E_1 = 26$ kcal/m, $E_2 = 49$ kcal/m) is greater than in the absence of equilibrium ($E_1 = 16$ kcal/m). These differences are caused by a slow reversible exothermic process, by which a less active form of oxygen in the bound state forms on the surface of the platinum, so having a poisonous effect. In the absence of equilibrium, this process, which is one of the slowest, tends almost entirely to discharge the platinum, and its influence disappears.

The Use of Radioisotopes for the Study and Control of Flotation Processes. I. N. Plaksin, S. P. Zaitseva, G. N. Khazinskaya and R. Sh. Shafeev, U.S.S.R.

The paper considers methods of studying flotation processes with radioisotopes and nuclear radiation.

Radioisotopes can be used for studying the fixation of flotation reagents on the surface of minerals where mono-molecular coverage of the surface is incomplete. Radiometric and microautoradiographic methods are used in this research.

The use of collector reagents containing radioisotopes has elucidated some causes of unsatisfactory passage into the froth of the most flotation-refractory sulphides, related to the material composition and structure of these minerals and the chemical bonds arising in their crystal lattices. The simultaneous use of radiometric and autoradiographic methods accompanied by solvent-washing of the mineral particles showed the conditions under wihch dixanthogenide and other products of the interaction of xanthogenates with sulphide minerals are formed.

The use of radioactive kerosene, and also of kerosene in conjunction with other flotation reagents made it possible to determine certain features of fixation on molybdenite depending on the kerosene concentration.

Contrast and track microautoradiography were used to study the distribution of sulphydryl collector

reagents on different particles of galenite in the flotation pulp. Their joint effect was also studied.

Combinations of xanthogenates of various alcohols produce a more even distribution on the galenite particles, and permit a more efficient use of reagents.

C^{14}-labelled tridecylamine was used to study the interaction of a cationic collector with hübnerite and wolframite. The investigation showed that the tridecylamine, when introduced into the flotation process, is substantially absorbed by a foaming product. Non-foaming products (quartz, fluorite, calcite) absorb insignificant quantities of reagent.

Nuclear Geophysics in Prospecting for Ore and Coal Deposits. Y. P. Bulashevich, G. M. Voskoboinikov and L. V. Muzyukin, U.S.S.R.

Nuclear geophysics is applied to ore and coal deposits principally in the form of exploratory bore-hole logging. Use of various types of logging with radiation sources is expanding steadily. Both the list of useful minerals which can be found by bore-hole logging, and the scope of the information yielded by the method, are on the increase.

The following types of radioactive or nuclear logging (RL) are in wide industrial use at Soviet ore and coal deposits: density or gamma-gamma logging (GGL) with a Co^{60} source; selective gamma-gamma logging (SGGL) with a soft-radiation source of the Se^{75} type; neutron-neutron logging (NNL) and neutron-gamma logging with a Po–Be neutron source; activation (particularly continuous activation) logging with the same source; and photo-neutron logging with the gamma-emitter Sb^{124}.

The chief purpose of RL at ore deposits is to distinguish ore bodies in the bore hole section, thus reducing assaying intervals, and to furnish on the site an approximate estimate of the useful content.

In coal deposits RL is used to determine the depth of the occurrence and the thickness and structure of the coal seams.

The GGL and SGGL methods are based on recording the scattered gamma radiation emitted by the source. Where the source emits sufficiently hard radiation and the sensitivity of the detector is low, the intensity of the scattered radiation is governed only by the density of the rock strata and the distance between source and detector. This applies to GGL, with which coal seams are distinguished by the maximum scattered-radiation levels. The essential feature of SGGL is the recording of the soft portion of the scattered-radiation spectrum, the intensity of which falls off steeply with an increase in the average atomic number of the elements in the medium. Its sensitivity is of the order of 0·01%, and it can be used successfully to distinguish ore bodies containing heavy elements (lead, tungsten, mercury, etc.), and also at iron ore (siderite) deposits.

The exceptionally large thermal neutron capture cross-section of boron enables boron ore bodies in the bore hole section to be distinguished by the NGL and NNL methods. Interference by water can be eliminated by inverse probes. These neutron methods, and similarly neutron-activation logging, have also been applied at deposits of copper, manganese, aluminium and various other ores.

Continuous-activation logging is appropriate where the occurring radioisotope has a suitable half-life. It is then possible to determine the optimum logging conditions (rate, length of probe, etc.) theoretically.

Neutron recording during photo-neutron logging makes it possible to distinguish ore bodies containing beryllium, and to estimate the beryllium content from 0·001% upwards.

Experience is confirming the effectiveness and economic expediency of nuclear geophysical methods in prospecting for ore and coal deposits.

Diffusion, Recrystallization and Phase Transformations. S. Z. Bokshtein, M. A. Gubareva, S. T. Kishkin and L. M. Moroz, U.S.S.R.

A method has been evolved for studying with radioisotopes the behaviour of grain boundaries in the process of plastic deformation and later recrystallization.

It has been shown that iron-recrystallization at relatively low (15%) and high (50–70%) degrees of deformation does not lead to any essential change in the location of the basic metal atoms situated on the boundary of the initial grains. When the metal structure changes considerably after recrystallization and also after polymorphous $\alpha \rightleftarrows \gamma$ transformation, the boundary atoms of the initial grains are not displaced to any great distance.

In the same way, impurity atoms (radioactive carbon) situated on the boundaries of the initial grain do not migrate across the boundaries of the new grains of recrystallized metal.

Plastic deformation, on the contrary, is accompanied by significant migration of the atoms situated on the grain boundary.

The data thus obtained show that the migration of grain boundaries during recrystallization and subsequent grain growth is associated with some specific mechanism differing from ordinary diffusion.

It has been shown that structural changes occurring in alloys at high temperatures can change the speed of the self-diffusion and hetero-diffusion processes. Thus when frequent eutectoid austerite $\rightleftarrows$ pulite transformation occurs in steel (0·8% C), the coefficient of iron self-diffusion is increased ten times.

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In the same way structural changes occurring in titanium during diffusion tempering hasten the diffusion process.

As a result of a study of the diffusion processes in titanium and its alloys in connexion with the polymorphous state, it has been established that the speed of the process in different titanium crystal variations alters greatly. At the temperature of polymorphous transformations the diffusion coefficient of tin in α-titanium is 2 orders of magnitude larger than in β-titanium. The activation energy of the diffusion in β-titanium is more than twice as great as in α-titanium.

This eliminates the previous contradiction between the high melting-point of titanium and the relatively low activation energy of the diffusion process in titanium. The well-known empirical ratio $Q = 40\ TS$ is maintained for titanium variation at high temperatures.

The Determination of the Thermodynamic Activity of Antimony in Alpha-Iron. I. A. TOMILIN, U.S.S.R.

The study of the solubility and thermodynamic activity of elements dissolved in solid iron is of interest in a number of metallographic problems. In order to ascertain the reasons for the decline of plasticity in iron alloys when antimony is present, it is important to know the thermodynamic characteristics of solid solutions of antimony in alpha-iron.

In this paper a method is suggested for determining the thermodynamic activity of antimony dissolved in alpha-iron, based on the study of antimony distribution between the two phases liquid lead and solid iron. The principle of the method is that a specimen of thin iron foil 10–30 μ thick and weighing about 0·1 g comes into contact with liquid lead containing a known concentration of antimony labelled with the radioisotope Sb^{124}. When this is kept at a given temperature antimony passes into the iron, spreading evenly through the whole thickness of the foil by diffusion. There is no appreciable change in the concentration of antimony in the lead. From the published thermodynamic data concerning the lead-antimony system, it is possible to estimate the activity of antimony in solid iron. The use of radio-antimony made it possible to measure precisely the concentration of this element in specimens weighing less than 0·1 g. It is exceedingly difficult to determine quantitatively the composition of weighed portions of this kind by ordinary chemical analysis. The Sb^{124} concentration was established from the gamma radiation with the use of a filter, which obviated the need to correct for internal absorption.

By the method described it was found that solid solutions of antimony in alpha-iron can be distinguished by positive divergences from the ideal state. Over a fairly wide range of concentrations, solutions of antimony in iron obey Henry's law.

Special experiments on the distribution of antimony between lead and liquid iron showed that in the liquid state also the iron-antimony system is marked by positive divergences from the ideal state when small concentrations of antimony are present.

The heat required for the solution of antimony in alpha-iron, and the excess partial molar entropy, were calculated from the activity temperature. The results were used for accurately locating the line showing the solubility limit of antimony in alpha-iron.

Since alloys of antimony with iron were obtained by diffusion saturation and not by cooling from the liquid state, there was no liquefaction. Thus the lattice constant of the alloys and its relation to the alloy concentration could be reliably determined. The solubility limit established from X-ray data agrees with that obtained with Sb^{124}.

Study of the Diffusion and Solubility of Various Ingredients in Germanium. E. G. MISELYUK, V. E. KOSENKO, L. A. KHOMENKO and V. D. IGNATKOV, U.S.S.R.

The diffusion process and solubility of the corresponding elements in germanium were studied with the radioisotopes Ag^{110}, Fe^{59}, Cd^{115}, Te^{127}, and Ta^{182}. It is interesting to study the diffusion and solubility of these elements in particular because their ingredient centres in germanium are electrically active, so that the conductivity and, more especially, the recombination of the current bearers, can be modified and the speed thus greatly increased. Studies were carried out with scintillation counters on monocrystalline germanium of high purity with a residual ingredient concentration of $\leqslant 5 \cdot 10^{12}$ cm^{-3} at a temperature range from 700 to 930°C.

The results were as follows:

1. The volume diffusion coefficients for Ag, Fe, Cd and Ta were found to be respectively (at 800°C) 8×10^{7}, $1{\cdot}6 \times 10^{-6}$, $4{\cdot}2 \times 10^{-12}$ and $6{\cdot}5 \times 10^{-13}$ cm^2/sec.

2. From the solubility temperatures their maximum values were fixed at $C_{Ag} = 1{\cdot}1 \times 10^{15}$ cm^{-3}, $C_{Fe} = 1{\cdot}5 \times 10^{15}$ cm^{-3}, $C_{Cd} = 4 \times 10^{18}$ cm^{-3}, and $C_{Ta} = 2 \cdot 10^{18}$ cm^{-3}.

3. The coefficient of surface diffusion for Ag was measured and proved to be higher than the volume diffusion coefficient by one order of magnitude at 850°C and six orders of magnitude at 200°C.

4. An intense evaporation of germanium, 2 orders of magnitude higher than in a vacuum, was observed in tellurium fumes.

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Measurement of Coefficients of Cation Self-diffusion in Silicate Melts by Means of the Radioisotopes Na^{24}, K^{42} and Ca^{45}. V. I. MALKIN and B. M. MOGUTNOV, U.S.S.R.

An important physico-chemical feature of an ionic melt is the mobility of its ions. Measurement of ion transport numbers in silicate melts showed that cation mobility considerably surpasses anion mobility, and that an ion's mobility tends to increase as its electrostatic field weakens. On the other hand, in melts containing two cations these were seen to exert on one another's mobility an effect closely related to the ratio of their co-ordination numbers.

In order more fully to appreciate the factors determining the effect of the interaction between the cations on their mobility, it is of interest to determine the absolute value of the cation mobility in melts containing a sodium ion in combination with other cations having the same silica concentration.

For this purpose the self-diffusion coefficients of the ions Na^+, K^+, and Ca^{++} were measured in the melts $Na_2O{\cdot}2SiO_2$, $Na_2O{\cdot}K_2O{\cdot}4SiO_2$, $Na_2O{\cdot}Li_2O{\cdot}4SiO_2$ and $Na_2O{\cdot}CaO{\cdot}4SiO_2$ by means of the radioisotopes Na^{24}, K^{42}, and Ca^{45}.

Experiments were carried out at 900–1200°C in alundum capillaries with a diameter of 5 mm and in graphite capillaries with a diameter of 3·5 and 8 mm, under the conditions of diffusion from a flat variable source in a semi-infinite space.

The distribution of radioactivity in the specimen was determined both by division into layers and by moving the specimen in relation to the window of a special lead chamber with a gas counter.

The method of determining the coefficients of self-diffusion was tried on the melt $Na_2O{\cdot}2SiO_2$. The experiments showed that the measurements do not depend on the substance of diameter of the capillary. This shows the virtual absence of surface diffusion and convection in the melts under study.

The measurements are accurate within $\pm 10\%$. The temperature ratio of the self-diffusion coefficient of the ion Na^+ in the melt $Na_2O + 2SiO_2$ can be described by the equation

$$D = 1{\cdot}82 \times 10^{-3}\, e^{-(11900/RT)}.$$

The value obtained for the self-diffusion activation energy coincides closely with the conductivity activation energy of the melt $Na_2O{\cdot}2SiO_2$ (12,000 cal/mole); and the value of the self-diffusion coefficient of the ion Na^+ calculated within 10% from the conductivity data tallies with the direct measurement. It follows that conductivity and diffusion in this melt have the same mechanism, and that the method used for measuring the coefficients of cation self-diffusion is reliable.

Addition to the melt of a second cation increases the self-diffusion activation energy of the ion Na^+ to 14,000 cal/mole in the melt $Na_2O{\cdot}4Li_2O{\cdot}4SiO_2$; 17,000 cal/mole in the melt $Na_2O{\cdot}K_2O.4SiO_2$; and 20,000 cal/mole in the melt $Na_2O{\cdot}CaO{\cdot}4SiO_2$.

The self-diffusion coefficient of the ion Na^+ in these melts decreases in the order

$Na_2O{\cdot}2SiO_2$; $Na_2O.Li_2O{\cdot}4SiO_2$; $Na_2O{\cdot}K_2O{\cdot}4SiO_2$; and $Na_2O{\cdot}CaO{\cdot}4SiO_2$.

Measurement of the self-diffusion coefficients of the ions K^+ and Ca^{++} in the melts $Na\,O{\cdot}K_2O{\cdot}4SiO_2$ and $Na_2O{\cdot}CaO{\cdot}4SiO_2$ showed that the ratio of the cation self-diffusion coefficients in these melts corresponds to that of their transport numbers. The results show that, when the two cations are combinad in various ways in the silicate melts, their mobility can be determined from the degree of structure condensation and also from the joint polarization of the anions by the two cations.

Dating by C^{14}. A. P. VINOGRADOV, U.S.S.R.

This report summarizes the results of studies made with two assemblies for dating geological and archaeological objects with C^{14}.

The advantages and drawbacks of three ways of determining C^{14} activity in solid, liquid and gaseous substances are discussed.

Data of the chemical preparation and cleaning of the gaseous carbon compounds ethane, acetylene and carbon dioxide, and the calculation of their C^{14} activity.

The report assesses the mistakes that can be made in determining age by C^{14}, and gives data for geological and archaeological objects in the Soviet Union.

Liquid Scintillators for Radiocarbon Dating in Archaeology. I. E. STARIK, S. I. RUDENKO, V. V. ARTEMEV, S. V. BUTOMO, V. M. DROZHZHIN and E. N. ROMANOVA, U.S.S.R.

A simple scintillator counter with one photomultiplier and no cooling is used for determining the absolute age of archaeological specimens with radiocarbon. Background is reduced by using a steel- and lead-laminated shield and amplitude pulse-height selection, and by making the detector from selected "clean" materials.

Ethyl benzene is synthesized from the carbon contained in the archaeological specimen.

From 18 to 72 ml of liquid scintillator was used in the measurements, corresponding to the introduction of 3–12 g of carbon from the specimen. With 40 ml of scintillator the background count speed and the contemporaneous carbon speed (without background)

were respectively 23·5 and 37 pulses per minute and with 70 ml, 28 and 57 pulses per minute. The statistical error of 48-hour measurements of specimens 5,500 years old is respectively 65 and 35 years with 40 and 70 ml of the scintillator.

Archaeological specimens from various regions of the Soviet Union were measured.

Tritium in Underground Water Studies. F. A. Alekseev, G. R. Golbek, V. N. Seifer, N. A. Vasileva, V. N. Maidebor, O. V. Sokolovsky and N. M. Shangin, U.S.S.R.

The authors show the development of the water indicator method, and the use of artificial and natural tritium for the study of underground water movement.

Two possible types of liquid movement on a seam were established: water seepage through the more pervious sections of the seam at speeds of 10–30 m a day; and the advance of the basic contour of pumped water on a relatively uniform part of the seam at a speed of 2 m a day. The latter movement corresponds to the movement speeds (1·9–2·2 m per day) calculated theoretically for a uniform seam. It is possible to estimate the flow quantitatively in movement of the first and second types. A method has been evolved for observing with tritium, water communication between the separate intercalations of the productive stratum of a petroleum seam.

A new method is proposed for controlling the exploitation of petroleum deposits by means of the natural tritium contained in surface water pumped into the seam both inside and outside the contour. The slow contour movement in large petroleum deposits with a sparse well network can be studied over long periods (about 10 years).

From the amount of decayed tritium in the water below the petroleum layer in working wells, the times and speeds of the contour water movement can be determined to within ± 1 year. Very little analysis (not more than 300–500 analyses per year on a large deposit) is necessary for following the contour movement.

A supersensitive apparatus has been evolved for measuring tritium in surface waters with liquid-filled standardized counters, and can be obtained by most industrial organizations.

Study of Carbon Isotope Exchange Reactions between Potassium Cyanide and some Carbonates, and their Use for Obtaining C^{14}-Labelled Potassium Cyanide. O. I. Andreeva and G. I. Kostikova, U.S.S.R.

The authors examine the results of a study on the isotope exchange of potassium cyanide with compounds differing greatly from it both in composition and structure, such as carbonates of alkaline and alkali-earth metals. The choice of these compounds, besides being of scientific importance, is also of practical interest, since carbonates are the starting materials which contain the isotope C^{14}, and cyanides are the key compounds used for the synthesis of labelled compounds.

The carbon isotope exchange reaction in the $KC^{12}N$—$BAC^{14}O_3$ system was studied at 600–800°C. The ratio between the components of this system and those given below agreed with the equimolecular ratio.

The authors show that at high temperatures complete exchange between these compounds can be secured. The exchange reaction begins when the cyanide melt is formed; later it occurs between the liquid and the solid phases, and its speed increases with temperature; at 800°C it is completed in 2 hours.

With carbonates of alkali metals the exchange reaction occurs in the melt and is completed at lower temperatures. Thus in the $KC^{12}N$—$Li_2C^{14}O_3$ system the exchange reaches 100% at 650°C, and in the $KC^{12}N$—$Na_2C^{14}O_3$ and $KC^{12}N$—$K_2C^{14}O_3$ systems at 700°C, in 2 hours.

The authors obtained cyanide-labelled potassium by the following method:

(1) the isotope exchange reaction $KC^{12}N$—$BaC^{14}O_3$ is produced at 800°C in 2 hr.
(2) the mixture $KCN + BaCO_3$ is separated by extracting the KCN with liquid ammonia in a circulating extractor.

By exchanging the equimolecular quantities KCN and $BaCO_3$, potassium cyanide is obtained with a chemical yield of more than 90% and a basic substance content of 96–97%. By using $BaCO_3$ with a high specific activity (60–70 mc/g), a KCN specific activity of over 80 mc/g may be obtained. The barium carbonate depleted of isotope C^{14} regenerates after the ammonia extraction without appreciable loss.

Study of the Isotope Effect in Hydrogen Exchange Reactions in Liquid Hydrogen Bromide and Liquid Ammonia. G. N. Avdulov, N. K. Semenova and I. F. Tupitsin, U.S.S.R.

The subject of the investigation was the thermodynamic isotope effects in naphthalene–hydrogen bromide and benzene-ammonia systems in the presence of potassium amide acting as a catalyst. Protium, deuterium and tritium atoms were present in the system during the experiments. The values of the distribution ratios for tritium exchange were

found to be: αTB_2—$C_{10}H_8$ = 4·0: 4·2 αNT_3—C_6H_6 = 0·60:0·63. The α values for deuterium exchange agreed with the data in the literature.

In the experiments on direct and "reverse" exchange, the kinetic isotope effects of hydrogen were measured in the liquid-phase systems hydrogen bromide–diphenyl and benzene–ammonia. The velocity constant in the exchange of tritium for protium atoms (K_T) is less than the velocity constant for deuterium exchange K_D: for exchange in liquid ammonia (K_D/K_T) = 1·3–1·6; in liquid hydrogen bromide (K_D/K_T) = 2–3.

The mechanisms of exchange reactions of aromatic hydrocarbons with HBr and NH_3 are considered with regard to the findings of kinetic experiments.

There is a brief description of the methods of preparation in which deuterized and tritiated compounds are used. For tritium counting a scintillation coincidence system was used; and spectroscopic and mass spectrometric methods were used for the isotopic analysis of deuterized substances.

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The Synthesis of Tritium-labelled Cyclic Hydrocarbons by Using Tritium Recoil Nuclei. A. N. Nesmeyanov, B. G. Dzantiev, V. V. Posdeev and Y. M. Rumyantsev, U.S.S.R.

The authors discuss the results of investigation of the interaction of tritium recoil atoms produced by the reaction $<i^6(n,\alpha)T$ with cyclohexane, cyclohexene, cyclohexadiene, methyl cyclohexane, cyclohexanol, cyclohexylammine and benzene.

Mixtures of these compounds with lithium carbonate were neutron-irradiated. From one gramme of lithium 4 mc of tritium was obtained per hour with a $4 \cdot 10^{12}/cm^2/sec$ neutron flux. The total yield of the products depends on the amount of tritium yielded by the crystals, and so on the irradiation conditions. The yield from the separate components is determined by analysis.

The irradiation products were analysed by vacuum distillation, using carriers and gas-liquid chromatography. The results obtained show that 20–40% of the tritium yielded by the lithium carbonate crystals is embedded in the parent molecule of the irradiated compound. When, for instance, cyclohexene is irradiated together with 22% of the labelled parent compound, 16% cyclohexane, 4% methyl cyclopentane and small amounts of other products are obtained.

The specific activity of cyclohexane and methyl cyclopentane separated on a chromatographic column may be high, and the only dilution is with products of radiolysis.

When other compounds are irradiated, there is a good yield only from the irradiated parent compound, and a small yield from other products. For purposes of preparation, cyclohexane and methyl cyclopentane are best obtained by irradiating cyclohexane; other cyclic hydrocarbons can be obtained by irradiating the compounds directly with lithium salts.

The paper describes a preparation column for separating tritium-labelled cyclohexane, cyclohexene and methyl cyclopentane from irradiated cyclohexene, and for separating the products yielded by the reaction of tritium recoil atoms with other cyclic hydrocarbons.

Method of Obtaining Sulphur-labelled Compounds by Reaction of "Hot" Sulphur-35 Atoms with Cyclic Hydrocarbons. B. G. Dzantiev and I. M. Barkalov, U.S.S.R.

The authors discuss methods of obtaining sulphur-labelled compounds, such as aliphatic and cyclic mercaptans and sulphides, by direct synthesis employing recoil atoms from the reaction Cl^{35} (n,p) S^{35}.

Hot S^{35} atoms were obtained in the middle of the target substance by exposing mixtures of CCl_4 and a cyclic hydrocarbon (cyclopentane, cyclohexane) to neutrons in a reactor.

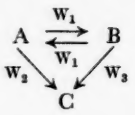
A method is given for irradiating the mixtures and then separating the various sulphur-bearing compounds by specific chemical methods, rectification, and paper and gas-liquid chromatography. The purpose of the exchange is clarified. The relation of the yield of the separated sulphur-labelled products to the composition of the mixture and type of exposure was investigated, and an active-sulphur balance settled. New types of atomic sulphur reactions were established: the CH_2: group is replaced and implanted on the C—C link. The cyclic molecule is destroyed in the interaction with the hot sulphur atoms. Hot sulphur atoms can initiate the formation of polymers containing sulphur. The yields of these reactions were established. Up to 98% of the active sulphur is linked in the form of organic sulphur compounds.

It was shown that sulphur-labelled thiophene, tetrahydrothiopyrane, cyclopentylmercaptan, cyclohexylmercaptan, ethyl-propyl-butyl-mercaptans, dicyclopentylsulphide, polymeric mercaptans and sulphides could be synthesized by heat. It is possible to regulate within broad limits the yield of various labelled compounds by changing the decelerating properties of the medium.

Study of the Mechanism of Various Heterogeneous Catalytic Processes with Carbon-14-labelled Compounds. G. B. Isagulyants and A. A. Balandin, U.S.S.R.

Most heterogeneous catalytic processes include a series of successive and parallel reactions. By using

isotopes in studies of the mechanism of heterogeneous processes, it is possible to make a direct estimate of the stages of the process at which an equilibrium is quickly established between the gaseous phase and the surface of the catalyst. In practice, transformations in complicated heterogeneous processes can often be reduced to the scheme:

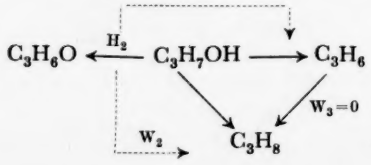


where A is the initial product, and B and C are products formed during the process.

It is evident that, if $W_2 = 0$, the formation of the product C is a consecutive process; whereas if $W_3 = 0$, the formation of B and C is parallel and independent. In many cases all the speeds are commensurate, and then the formation of product C is consecutive and parallel. Formulae are obtained for calculating the separate speeds in the scheme from experimental determination of the changes in the concentrations and specific activity of the products A, B and C for various times of contact.

The dehydrogenation reaction of butane towards butadiene on a chromium catalyst is in practice a purely consecutive process, and all the butadiene is formed by dehydrogenation of the butylene which has formed and separated in the mass.

The disintegration of isopropyl alcohol on vanadium trioxide is an example of a purely parallel reaction. Dehydrogenation and dehydration of the alcohol occur, but in the reaction products there is relatively little propylene and much propane. The latter can be formed as a result either of propylene hydration or of hydrogenolysis of the alcohol:



Experiments showed that propylene hydration does not occur with various contact times at a temperature of 315°C, and all the propane is formed by hydrogenolysis of the isopropyl alcohol.

A more complicated process, where parallel and consecutive reactions occur simultaneously, is the formation of ethylene when ethyl alcohol is dehydrated on aluminium oxide and a sulphate catalyst. It is accompanied by the formation of a considerable amount of diethyl ether.

The process was studied at temperatures from 275 to 450°C.

At high temperatures (350–400°C) up to 80% of the ethylene is formed from the alcohol and little is formed consecutively. As the temperature decreases, the ethylene formed consecutively grows, and a 275°C reaches 60%. On an alumopotassic sulphate catalyst at 275°C the basic ethylene mass is formed directly from the alcohol.

The reciprocal transformation rates of the alcohol and the ether as a rule greatly exceed those of their transformation into ethylene; this made ethylene formation a difficult problem in earlier experiments based on purely kinetic studies.

The method also gave positive results when used in coal formation studies when alcohol is degraded on dehydrating catalysts, and for the study of the mechanism of the dehydrogenation of cyclohexane into benzene.

Reduction of Promethium on a Mercury Cathode. A. K. Lavrukhina, G. M. Kolesov, Tan Syao-en, U.S.S.R.

It is well known that, of all the rare-earth elements, only Yb, Eu and Sm can be reduced to a bivalent state and so separated on a mercury cathode from electrolytes containing complex-forming additives. The authors observed the separation of radioactive promethium on a mercury cathode with samarium, which showed that it can be reduced to a bivalent state.

Using radiochemically-pure Pm^{147}, the authors made a detailed study of the influence of a series of factors on the extent to which promethium passes into an amalgam. The experiments were carried out in an electrolyte cell containing 10 ml of a solution, of 0·116 M potassium citrate at pH 5·9, and a temperature of 0–+2°C. 200 g of purified mercury were used as a cathode. A coil of platinum wire was used as an anode. The mercury and the electrolyte were mixed at a speed of 500 r.p.m.

It was shown that radioactive promethium only passes into the mercury cathode if the current is relatively dense (above 50 mA/cm²) and when rare-earth elements such as ytterbium and samarium, which have a stable bivalent state, are present in the electrolyte. Electrolytic separation of the promethium is not observable until formation of the mixed potassium and samarium amalgam. The promethium then passes into the amalgam up to 85%.

When the current is denser (100 mA/cm²), a notable difference may be observed in the transition speed of the promethium and samarium. Most of the samarium passes into the amalgam during the first 30 minutes; but the promethium does not begin to

separate on the mercury cathode until 45 minutes after the commencement of electrolysis.

The promethium separation is mainly affected by the nature of the alkali metal contained in the electrolyte. With lithium, the degree of promethium transition does not depend on the presence of another rare earth element or the citrate ion concentration. This confirms the occurrence of electrolytic reduction of promethium in electrolysis with a mercury cathode at high current densities.

Separation of the promethium into the mercury cathode goes through the stage of its reduction to a bivalent state with formation of the amalgam with the alkali metal:

$$Me^{+} + e^{-} \rightleftarrows Me(Hg)$$

where Me^{+} is the cation of the alkali metal,

$$Pm^{3+} + e^{-} \rightleftarrows Pm^{2+}; \qquad Pm^{2+} + 2e^{-} \rightleftarrows Pm(Hg).$$

The authors also studied the behaviour of cerium and erbium. Cerium separates on a mercury cathode under the same conditions as promethium. On the other hand, erbium virtually does not separate.

From the results of this study and all the published data, the authors conclude that promethium and other elements of the cerium group can be reduced to a bivalent state under certain conditions of electrolysis.

Method of Obtaining Concentrated Preparations of Cl^{36} and Br^{82} by Recoil Nuclei under Exposure to Highly-condensed Neutron Fields. L. N. KURCHATOVA and B. V. KURCHATOV, U.S.S.R.

The classical Szilard-Chalmers method for obtaining concentrated radio-active preparations is usually considered rather ineffective when large integral neutron fluxes are used, because of the considerable disintegration of the compound under irradiation.

The authors found compounds of bromine and chlorine with carbon which made it possible to considerably enrich the chlorine and bromine in radio-isotopes by means of recoil nuclei during exposure to neutron fluxes of the order of 10^{13} neutrons/sec cm^2.

These compounds correspond to the formula CnX, where X = Cl or Br, and n = 10–20 for chlorine compounds and 25–70 for bromine compounds. They are fairly stable thermally and chemically. The compound $C_{30}Br$ withstands heat up to 300°C in an argon atmosphere without detachment of bromine; it disintegrates completely at a temperature of 600°C. It is practically unaffected by reducing agents in aqueous solution.

The chlorine and carbon compounds are about as stable as the bromine and carbon compounds. Only strong reducing agents (e.g. solution of the sulphate $CrSO_4$) slowly detach the chlorine from the compounds of chlorine and activated carbon at room temperature. Enrichment of bromine in Br^{82} with these bromine and carbon compounds goes up 50–500 times in integral fluxes of the order of $5 \cdot 10^{17}$ neutrons/cm^2. The specific activity of the concentration fluctuates between 6 and 35 mc/mg of bromine, and will probably be raised by improvement of the method. The structure of the compound ensures a good extraction of radioactive bromine (up to 75%) by a very simple technique.

The carbon + chlorine iron + chlorine system proved the most effective for obtaining concentrated chlorine-36. By this system an enrichment factor of 6–20 was obtained, with a specific activity of the concentrate of 230–55 mc/g chlorine.

The concentration effect when these chlorine and bromine compounds are exposed to neutrons is the cumulative result of a number of processes: formation of radioactive chlorine atoms, radiolytic detachment of the halide, diffusion of the products in the carbon lattice, their absorption on the surface, and their recombination at various centres. Many factors, such as the ultramicroscopic structure; the nature of the new compounds, related in type to the surface compounds; the presence on the carbon surface of centres with a continuous sorption energy spectrum; the probable formation, through carbon irradiation, of various stationary recombination centres, and others, constitute an extraordinary variety of conditions for the formation and interaction of irradiation products with the carbon skeleton and surface. Therefore these systems open the way to a wide range of experiments to select the ideal conditions for enrichment.

A Thermic Method of Preparing Sr^{90} Sources. N. I. BOGDANOV, P. V. ZIMAKOV, K. P. ZAKHAROVA and V. V. KULICHENKO, U.S.S.R.

Sources of ionizing radiation based on the radioisotope Sr^{90} are widely used in apparatus and systems of automatic control and regulation of industrial processes.

The technology of the preparation of sources is based on dehydration of a mixture of a radioactive solution of strontium nitrate with components such as boric anhydride, silica, and alumina.

Thermic treatment of the dehydrated mixture at a high temperature produces a very mobile melt. This cools to a vitreous mass containing the required quantity of the radioisotope Sr^{90}.

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The paper gives data and discusses the results of dehydration of the system $SrO—B_2O_3—SiO_2$ within a temperature range of 100–1000°C, and justifies the choice of the main parameters of the technological process. It summarizes a method of mounting a vitreous preparation containing the required quantity of the radioisotope Sr^{90} on bases of various shapes and sizes made of steel, ceramic and other materials.

The authors discuss the main parameters ensuring that various types of sources shall be reliable and safe in operation, and give data of Sr^{90} sources prepared by the thermic method.

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forthcoming papers

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W. C. DEWEY and W. K. SINCLAIR: Criteria for evaluating collimators used in *in vivo* distribution studies with radioisotopes

HERBERT E. SKIBITZKE, HOWARD T. CHAPMAN, GERALDINE M. ROBINSON and RICHARD A. MCCULLOUGH: Radio-tracer techniques for the study of flow in saturated porous materials

LEONARD A. WALKER, GERALD SPARLING and HELEN MERCER: A simple method for the differential counting of radioactive iron (Fe^{59}) and chromium-51 in mixtures

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W. RALPH SINGLETON, ALAN CASPAR and WALTER S. FLORY, JR: A cobalt machine for semi-acute irradiation of growing plants

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R. C. PALMER, D. K. DAVIS and W. V. WILLIS: A remote sampling system for high-level gamma sources (Technical Note)

F. J. CARLETON and H. R. ROBERTS: Determination of the specific activity of tritiated compounds on paper chromatograms using an automatic scanning device